MECHANISTIC AND SITE ISOLATION STUDIES OF TRANSITION METAL OXIDATION CATALYSTS

By

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To Susan, Jean, Mitch and Pat Pribich

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

MECHANISTIC AND SITE ISOLATION STUDIES OF TRANSITION METAL OXIDATION CATALYSTS

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Mechanistic work reported here involves the investigation of the oxidation of 1-hexene to 2-hexanone catalyzed by Rh(III)/Cu(II) mixtures. A number of results are obtained that indicate that $[Rh(CO)_2Cl]_2$ as a catalyst precursor must be converted to a rhodium(III) complex before catalysis occurs. The oxidation of the rhodium(I) precursor to the active rhodium(III) catalyst in the absence of copper is reported in detail. An unusual mechanism results which involves the in situ production of hydrogen peroxide from the alcohol solvent reduction of O_2. The hydrogen peroxide then oxidizes $[Rh(CO)_2Cl]_2$ to an unstable [Rh(CO)(OOH)(?)]

intermediate. This oxidation occurs only in solvents capable of reducing O_2.

Cofunctionalization of silica gel with trialkylchlorosilanes and $(CH_3O)_3SiCH_2CH_2CH_2SRh(CO)_2$ produces a catalyst for the oxidation of 1-hexene that can be compared with a catalyst that does not have an R_3Si- covering. Physical methods are used to determine the concentration of groups on the silica surface and also to determine the loading at which site separation occurs. The alkylated supports can be loaded with a greater concentration of the site-isolated rhodium complex producing catalysts which have greater activity per gram of catalyst and longer lifetimes than the corresponding catalysts produced with non-alkylated silica gels. Increasing the length of the alkyl group used to cover the surface decreases the effectiveness of the silica as a catalytic support and eventually leads to a catalyst surface that is not wetted by ethanol solvent.

A three nitrogen, two oxygen salen-type ligand was successfully synthesized on silica gel. Cobalt, copper, manganese and iron metal ions were incorporated into the supported ligand system. The iron(III) and manganese(II) systems achieved oxygen atom transfer from iodosylbenzene to a cyclohexene substrate producing different product ratios than homogeneous tetraphenylporphyrinato metal systems have yielded and are also the first supported systems to achieve this process.

Several other results are reported, including the preparation of an air sensitive iron(II) silica gel bound complex, incorporation of copper into the silica gel matrix, preparation of a silica gel based anion exchange resin, and examination of titanium carbide as a catalytic support.

CHAPTER I
GENERAL INTRODUCTION

The efficient conversion of ubiquitous substances on this planet into other useful species is a desirable and perhaps even honorable goal which correspondingly attracts the efforts of large segments of the scientific community. Specifically, a subset of this broad area is the efficient catalytic use of naturally occurring dioxygen via interaction with transition metal centers. The following chapters will describe investigations which in some way involve this area of research. A rather detailed study on the formation and nature of a specific homogeneous rhodium oxidation catalyst is presented in the second chapter.

The general interest in the Chapter II catalyst led to work which supported the catalytic system on an inorganic polymeric solid. Subsequent efforts to maximize the efficiency of this supported system while gaining detailed information on the support medium itself are represented in the third chapter.

A general broadening of study to include different metals, ligands, substrates and even solid supports led to further research; the various results of which are detailed in the fourth chapter.

Specific background information and introduction is included with each topic as it is discussed. The general introduction provided by this brief overview should then allow comprehension of the pattern of research on interrelated topics presented in the following.

CHAPTER II
THE SPECIFIC OXIDATION OF $[Rh(CO)_2Cl]_2$ BY O_2 VIA THE COORDINATION OF IN SITU GENERATED HYDROGEN PEROXIDE

Introduction

Homogeneous catalysis has developed rapidly during the last twenty years as organometallic chemistry has been firmly established as a major discipline within inorganic chemistry. The search for new and more efficient catalysts was intensified as the finite nature of the crude oil supplies which provide the feedstocks of many important chemical processes was more closely realized. Oxidations have specifically received much attention; there have been estimates that an oxidation step is involved in the production of over 50% of the chemicals manufactured industrially.[1] Water, alkylperoxides and dioxygen are frequently used as oxidation reagents. Dioxygen is the most desirable one, not only due to its obvious availability, but also because of its favorable energetics.

Homolytic and heterolytic are the two major categories into which metal catalyzed homogeneous oxidations have most often been divided.[2,3] Homolytic oxidations are those in which radical intermediates are produced during the oxidation process. However, the drawback of most radical processes is a lack of product selectivity, and that is also a major problem in these oxidations. One reason for this lack of specificity is that in many homogeneous metal catalyzed oxidations of hydrocarbon by O_2 the metals are involved in just the first step of reaction.[4-9] These metals decompose peroxides and thus initiate free-radical autoxidations. These free radicals then react with substrates such as olefins leading to the formation of several products.

Heterolytic oxidations, also known as nonfree-radical oxidations, involve binding of a substrate to a metal center, rearrangement, and later release of products. The Pd/Cu catalyzed oxidation of ethylene to acetaldehyde in the presence of water[10] (the Wacker process) is one well-studied example. The systems which undergo this type of oxidation have been the focus of much research aimed at adjusting the metal centers in order to improve catalytic activity. This has been especially true since the discovery of Vaska's complex, $Ir(P(C_6H_5)_3)_2(CO)Cl$, and the realization that it is able to reversibly bind dioxygen.[11] This "oxygen-atom transfer process" does not involve free radicals and results in product specificity. Since Vaska's complex was discovered several O_2 oxidations of non-organic substrates have been

judged to occur by the O-atom transfer process.[12-19] General knowledge of this type of reaction is largely dependent upon the ability to procure detailed mechanistic information. A mechanistic investigation of one reaction will be presented in the following sections.

Background

Considering specifically rhodium catalyzed oxidations of hydrocarbons by dioxygen, several examples have been reported which seemingly do not proceed by either free radical or simple Wacker processes.[20-24] One of these is the rhodium/copper co-catalyzed oxidation of terminal olefins to 2-ketones with $\geq$ 98% specificity[20] (reaction 1).

$$2CH_2{=}CHR + O_2 \rightarrow 2CH_3C(O)R \qquad (1)$$

The Wacker-Smidt process refers to the palladium(II)/-copper(II) co-catalyzed oxidation of olefins to ketones and aldehydes using water as the direct oxidant.[25-26] Palladium(0) is produced as an intermediate in this process, and the copper(II) is necessary to oxidize it back to Pd(II), the active catalyst. Only a stoichiometric reaction occurs and Pd(0) metal is produced if no Cu(II) is used. The general steps of the mechanism and the net reaction are shown

below (reactions 2-5) for the catalytic oxidation of ethylene to acetaldehyde.

$$Pd(II) + H_2O + CH_2{=}CH_2 \rightarrow Pd(0) + H_3CCHO + 2H^+ \quad (2)$$

$$Pd(0) + 2Cu(II) \rightarrow Pd(II) + 2Cu(I) \quad (3)$$

$$2Cu(I) + 1/2\ O_2 + 2H^+ \rightarrow 2\ Cu(II) + H_2O \quad (4)$$

$$\text{Net: } CH_2{=}CH_2 + 1/2\ O_2 \rightarrow CH_3CHO \quad (5)$$

Water is the direct oxidant here, even though O_2 is consumed. Dioxygen is reduced to H_2O by Cu(I), which reforms the Cu(II) necessary for oxidizing Pd(0) to Pd(II). Other processes which are thought to proceed in a similar manner are referred to as having a "Wacker" mechanism.

Mimoun and co-workers put forth great effort to rule out a Wacker-type mechanism for reaction 1. Several experimental observations could not be rationalized by a Wacker mechanism.[20] Thus, despite apparent similarities between Mimoun's system and the earlier rhodium/copper catalyzed system which is reported to have a Wacker-type mechanism,[27] the differences are great enough to rule out the hydrolysis process found in Wacker chemistry for Mimoun's system.

Mimoun proposed that the catalyst in the Rh(III)/Cu(II) oxidation system is a rhodium(I) complex produced from the ethanol reduction of $RhCl_3$ and Cu(II) in the initiation step shown in reaction 6.

$$RhCl_3 + 2CH_2{=}CHR + Cu(ClO_4)_2 + 1.5CH_3CH_2OH \rightarrow [Rh(CH_2{=}CHR)_2]ClO_4 + CuCl_{(s)} + HClO_4 + 2HCl + 1.5\ CH_3CHO \quad (6)$$

The observations which lead to this proposal by Mimoun are the following: (1) active catalysts are formed by using $[Rh(C_8H_{14})_2Cl]_2$ in the presence of 2 equivalents of HCl instead of $RhCl_3 \cdot 3H_2O$; (2) an amount of acetaldehyde approximately equal to the moles of catalyst used is produced from ethanol oxidation at the beginning of the catalytic reaction; and (3) 85% of the Cu(II) precipitates as CuCl at the beginning of the catalytic 1-hexene oxidation. Initiation of the catalysts would then be possible by the binding of dioxygen to the reduced rhodium species. From reaction 6 it can be seen that there are at least two possible needs for an equivalent of Cu(II) to produce the best catalytic conditions. The copper(II) is either necessary for the reduction of $RhCl_3 \cdot 3H_2O$ to Rh(I) with the stoichiometric production of CuCl, or for the removal of chloride ion from solution to yield a more unsaturated rhodium center. A combination of both roles for copper is possible, and Mimoun did not eliminate some other possible need for copper.

The mechanism Mimoun proposed involves a metal centered oxygen atom transfer involving coordination of dioxygen and

olefin to the rhodium(I) cation from reaction 6, a rearrangement to a peroxometallocycle, and then a decomposition to the rhodium(I) complex and the oxidation products. Figure 1 shows this mechanism. It was based upon Mimoun's suggestion that the active catalyst was a rhodium(I) complex that led to the preparation of a silica gel organosulfide supported rhodium(I) complex. This heterogenized complex produced an active and stable catalyst for the oxidation of 1-hexene to 2-hexanone[28] (vide infra, Chapter III).

Results and Discussion

Characterization of the Catalyst as a Rhodium(III) Chloride Complex

The rhodium carbonyl dimer (A), $[Rh(CO)_2Cl]_2$, was selected as the catalyst precursor due to the facile loss of the CO ligands in the presence of O_2, the presumed need for a rhodium(I) catalyst to coordinate O_2 and olefin, and the usefulness of the CO ligands for infrared analyses. Employing A as a homogeneous catalyst for reaction 1 at various chloride concentrations and in the presence of Cu(II) at 70°C, the data in Figure 2 were obtained. Note that the maximum initial 1-hexene oxidation rate (indicated by the amount of 2-hexanone produced) is achieved using a chloride/rhodium mole ration of 3:1, as was originally

Figure 1. The mechanism proposed by Mimoun to account for the Rh(III)/Cu(II) catalyzed O_2 oxidation of 1-hexene to 2-hexanone.

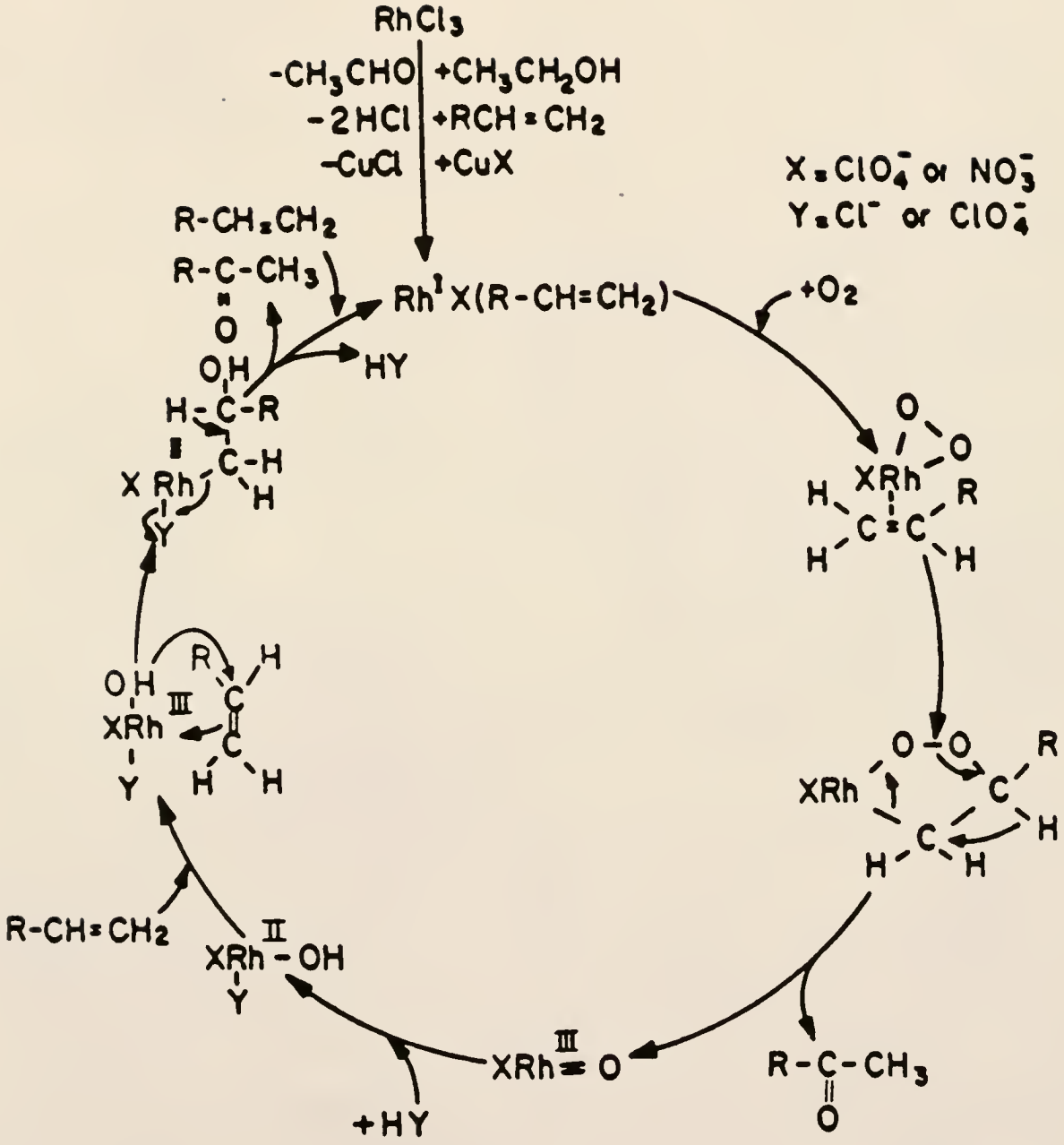
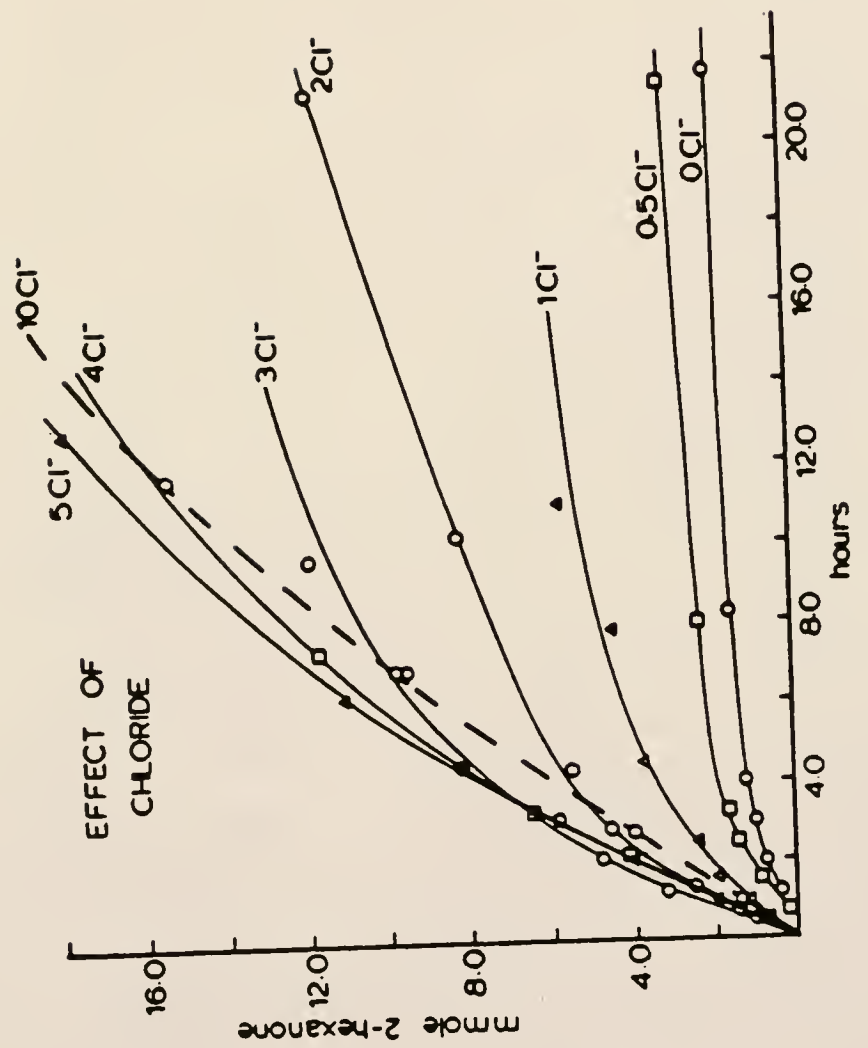

RhCl3
-CH3CHO +CH3CH2OH
-2HCl +RCH=CH2
-CuCl +CuX
X=ClO4- or NO3-
Y=Cl- or ClO4-
R-CH=CH2
R-C-CH3
O
OH
H-C-R
C-H
H
X Rh
Y
HY
Rh^I X(R-CH=CH2)
+O2
O
O
XRh
H
C=C
R
H
O
O
R
XRh
C
H
C
H
H
R-C-CH3
O
XRh^III=O
+HY
XRh^II-OH
Y
R-CH=CH2
OH
XRh^III
Y
R
H
C
C
H
H

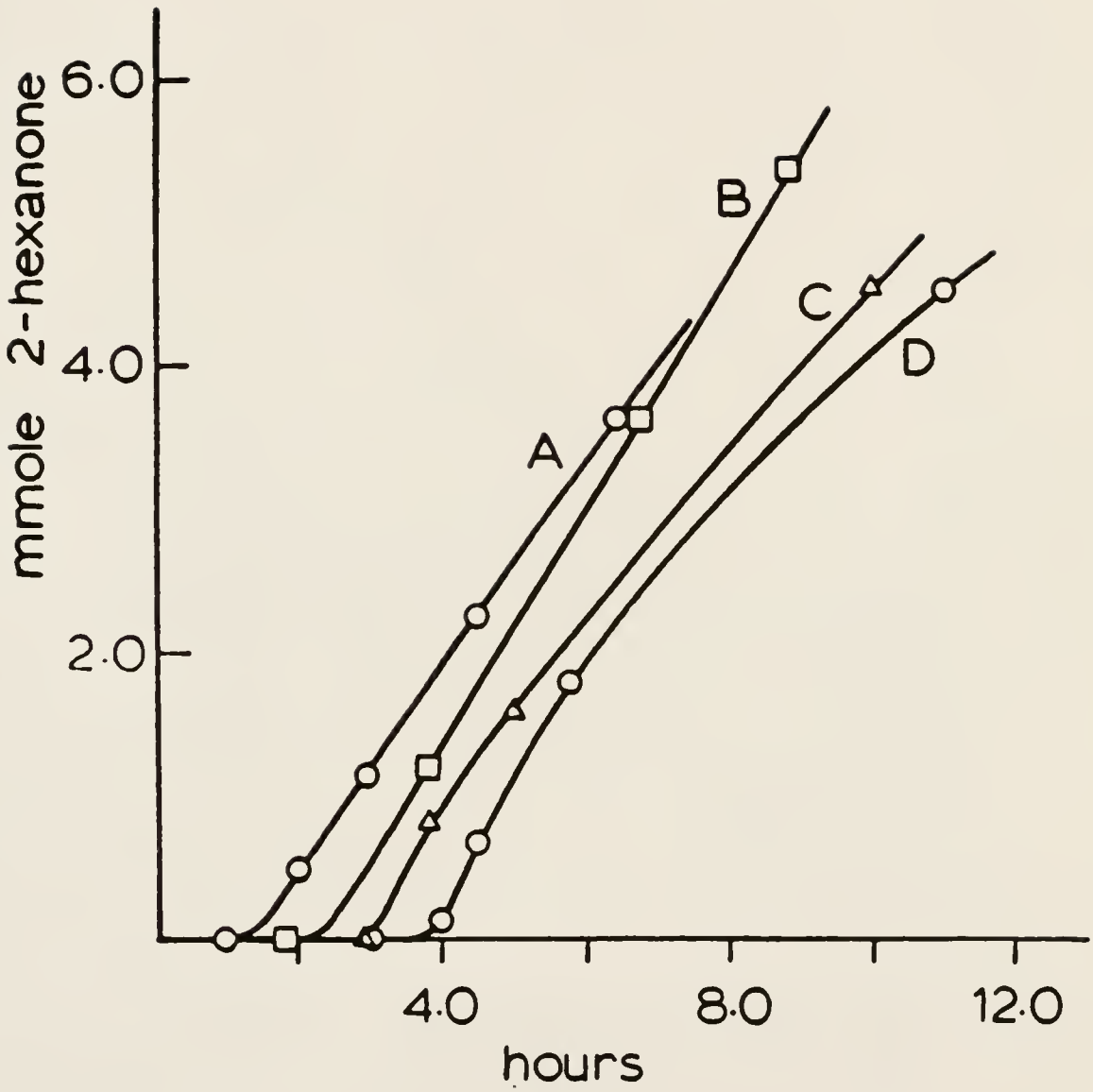
Figure 2. Effect of increasing the chloride/rhodium ratio on the initial rates and catalyst stabilities for the O_2 oxidation of 1-hexene at 70 C and 52 psi O_2, in the presence of one equivalent of Cu(II).


EFFECT OF
CHLORIDE
10Cl⁻
5Cl⁻
4Cl⁻
3Cl⁻
2Cl⁻
1Cl⁻
0.5Cl⁻
0Cl⁻
mmole 2-hexanone
16.0
12.0
8.0
4.0
4.0
8.0
12.0
16.0
20.0
hours

reported for this system at 40°C. However, increasing the chloride/rhodium ratio to 5:1 at 70°C causes a considerable increase in catalyst stability with little change in the initial rates, in contrast to the result obtained at 40°C, where a large drop in activity was found for the 5:1 ratio. (For example, after 20 h at 70°C with a 3:1 Cl/Rh mole ratio, the catalytic activity is only 7.5% of the initial value, while after the same time period with a 5:1 Cl/Rh ratio the activity is 34% the initial rate.) Increasing the chloride/rhodium ratio to 10 causes an even further increase in catalyst stability at 70°C (the activity after 20 h is 51% of the initial rate). A similar beneficial effect of increasing the Cl:Rh ratio to 5:1 was observed in analogous experiments with Cu(II) absent. This suggests that a specific interaction of chloride with rhodium and not copper leads to catalyst improvement. Furthermore, the marked dependences of both initial rate and catalyst stability on such large chloride concentrations suggest a rhodium(III)-chloride interaction. These results, along with others to be presented, indicate that a rhodium(III) chloride complex is the catalyst or the immediate precursor.

Experiments were conducted investigating the effect of dioxygen pressure on 1-hexene oxidation at 70°C. The use of $[Rh(CO)_2Cl]_2$, H_2SO_4 and NaCl to catalyze the production of 2-hexanone from 1-hexene can be accomplished in the absence of Cu(II). These results, along with the existence of an induction period, are shown in Figure 3. Also demonstrated

Figure 3. Demonstration of the dependence of the length of the induction period on the pressure of O_2, in the absence of Cu(II) at 70 C, using $[Rh(CO)_2Cl]_2$ as the precursor. The O_2 pressures are for A, 3.7 atm; B, 1.9 atm; C, 1.4 atm; and D, 1.0 atm.


mmole 2-hexanone
6.0
4.0
2.0
A
B
C
D
4.0
8.0
12.0
hours

is the first-order dependence of the induction period on dioxygen pressure. During the induction period the solution color changes from light yellow (the color of $[Rh(CO)_2Cl]_2$) to bright orange (normal for rhodium(III) chloride complexes).[29] No induction period is seen when $RhCl_3 \cdot 3H_2O$ is used rather than A, nor when 0.1 equivalent or more of Cu(II) is added to the reaction mixture. A proposal suggested by these experiments is that of the dioxygen oxidation of $[Rh(CO)_2Cl]_2$ to a rhodium(III) chloride complex (which is either the active catalyst or an immediate precursor) during the induction period.

Further investigation of this system involved the reaction of A, dioxygen, and HCl in ethanol, at 40°C in the absence of 1-hexene substrate. A bright orange complex (C) was isolated as $RhCl_3(H_2O)_2 \cdot CH_3CH_2OH$ after 12 hours of reaction. This process is described by reaction 7.

$$[Rh(CO)_2Cl]_2 + 4HCl + 2O_2 + 4CH_3CH_2OH \rightarrow 2RhCl_3(H_2O)_2 \cdot CH_3CH_2OH + 2CH_3CHO + 4CO \quad (7)$$

The rhodium product (C) was characterized by elemental analysis, molecular weight determination, and its infrared and visible spectra.[30] The stoichiometry for reaction 7 was verified in both $[Rh(CO)_2Cl]_2$ and HCl, but this was not possible for O_2, CH_3CH_2OH, and CH_3CHO due to the catalysis of reaction 8 by C (vide infra). The addition of an equivalent

$$2CH_3CHROH + O_2 \rightarrow 2CH_3CRO + 2H_2O \qquad (8)$$

$$R \equiv CH_3 \text{ or } H$$

of Cu(II) or the use of $[Rh(C_8H_{14})_2Cl]_2$ as the rhodium(I) precursor considerably speeds up reaction 7 (vide infra) but does not affect its outcome. Compound C catalyzes the oxidation of 1-hexene to 2-hexanone as efficiently as $RhCl_3 \cdot 3H_2O$ and without the occurrence of the induction period observed when using $[Rh(CO)_2Cl]_2$ as the catalyst precursor under identical conditions (see Figure 3). The observed solution color changes and other results described above indicate that under reaction conditions for the catalytic oxidation of 1-hexene (reaction 1), the rhodium(III) complex (C) is produced from the oxidation of $[Rh(CO)_2Cl]_2$. An explanation for the role of copper(II) and a more detailed study of reaction 7 will be discussed in the second part of this chapter.

To rule out the possibility that $RhCl_3 \cdot 3H_2O$ (or C) may be subsequently reduced to a rhodium(I) complex by alcohol solvent to initiate catalysis (as proposed by Mimoun in reaction 6), we investigated the initiation step using $RhCl_3 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$ as precursors. For our study we chose isopropyl alcohol as solvent since upon oxidation this alcohol forms acetone which is much easier to quantitatively measure than the more volatile acetaldehyde (produced from ethanol). Using GLC, we found that in the

presence of 1 equivalent of Cu(II) only 0.5 equivalents of acetone is produced immediately on mixing all reagents necessary for the catalytic oxidation of 1-hexene and that its concentration remains constant for at least 0.5 h. From this result we can rule out the simultaneous reduction of Rh(III) and Cu(II) proposed in reaction 6 because this would require the oxidation of 1.5 equivalents of isopropyl alcohol. We propose that reaction 9 initiates the catalytic cycle for this system

$$Cl^- + Cu^{2+} + 0.5(CH_3)_2CHOH \xrightarrow[\text{isopropyl alcohol}\\ \text{1-hexene}]{\text{1 atm } O_2 \text{ at } 40^\circ C} CuCl_{(s)} + 0.5(CH_3)_2CO + H^+ \qquad (9)$$

when $RhCl_3 \cdot 3H_2O$ is used as the catalyst precursor. Our proposal requires that only enough reducing equivalents are provided by isopropyl alcohol for the reduction of Cu^{2+} to form CuCl. Copper(I) chloride may be isolated from the reaction mixture in 85% yield without affecting the catalytic oxidation.

Mechanism of the O_2 Oxidation of $[Rh(CO)_2Cl]_2$ to Rhodium(III) Chloride

The oxidation of $[Rh(CO)_2Cl]_2$ (A) to rhodium(III) trichloride (C) by O_2 was originally studied because of our interest in characterizing the active catalyst for the Rh/Cu-co-catalyzed 1-hexene oxidation (reaction 1). Copper(II) was excluded in these initial investigations to facilitate the interpretation of the electronic absorption spectra, elemental analysis and molecular weight data. The substrate 1-hexene was excluded from these solutions to avoid its catalytic oxidation to 2-hexanone after the formation of the rhodium(III) chloride product. As described in the previous section, the exclusion of Cu(II) and 1-hexene during these studies proved to be quite useful for characterizing the rhodium catalyst. The oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride was generally monitored by electronic absorption spectroscopy in order to determine the reaction's end point. In the course of these studies it was found that at elevated O_2 pressures (3-5 atm) an unusual intermediate exhibiting a visible absorption band at 385 nm could be detected. This observation led to a detailed investigation of the mechanism of the O_2 oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) chloride in reaction 7, and the results are presented below.

The electronic spectral changes accompanying the oxidation of the $[Rh(CO)_2Cl]_2$ (A) to rhodium(III) chloride (C) in the absence of both Cu(II) and 1-hexene is shown in

Figure 4 as a series of spectra recorded over the course of the reaction. The growth and decay of an intermediate (B) with an absorbance at 385 nm is noted. The charge-transfer band beginning at the shortest wavelength is a result of A, while the band at 480 nm is produced by C. As shown in Figure 5, intermediate B is more stable in the presence of excess Bronsted acid ($8HClO_4/A$). The presence of two isosbestic points (at 377 and 435 nm) in both Figures 4 and 5 suggests the formation and subsequent reactivity of only one intermediate. The isosbestic point at 377 nm is a result of the reaction of A to form B at the beginning of reaction 7 (before much final product C has been formed). Early in the reaction the decomposition of B to C becomes quite pronounced, and this point disappears. The second isosbestic point emerges at 435 nm when all A has been consumed and results from the exclusive reaction of B to form C.

The initial rate of formation of B was found by visible spectroscopy to follow the rate expression shown in eq. 10,

$$\frac{-d[A]}{dt} \text{ or } \frac{-d[B]}{dt} = k[H^+][O_2] \qquad (10)$$

which is independent of the concentration of A. The zero-order dependence on [A] rules out a mechanism involving initially the formation of a rhodium hydride followed by the insertion of dioxygen to form a rhodium hydroperoxide intermediate, which occurs with $K_2[RhH(CN)_4(H_2O)]$,[31e] and is

Figure 4. Series of visible spectra resulting from the O_2 oxidation of $[Rh(CO)_2Cl]_2$ at 40°C in the absence of any $HClO_4$. Initial $Rh(CO)_2Cl_2$ is 0.98×10^{-3} M. Spectra were recorded over a 12 hour period.

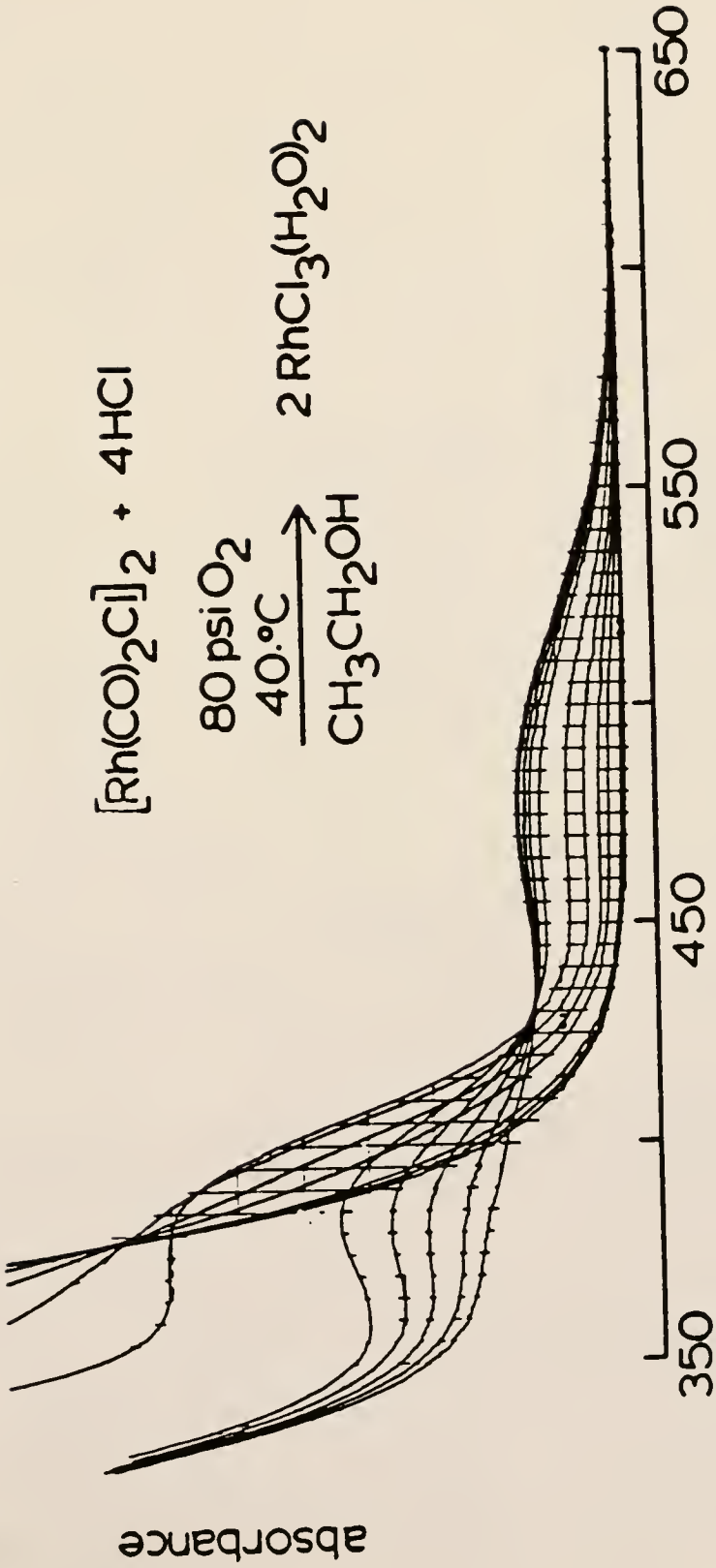
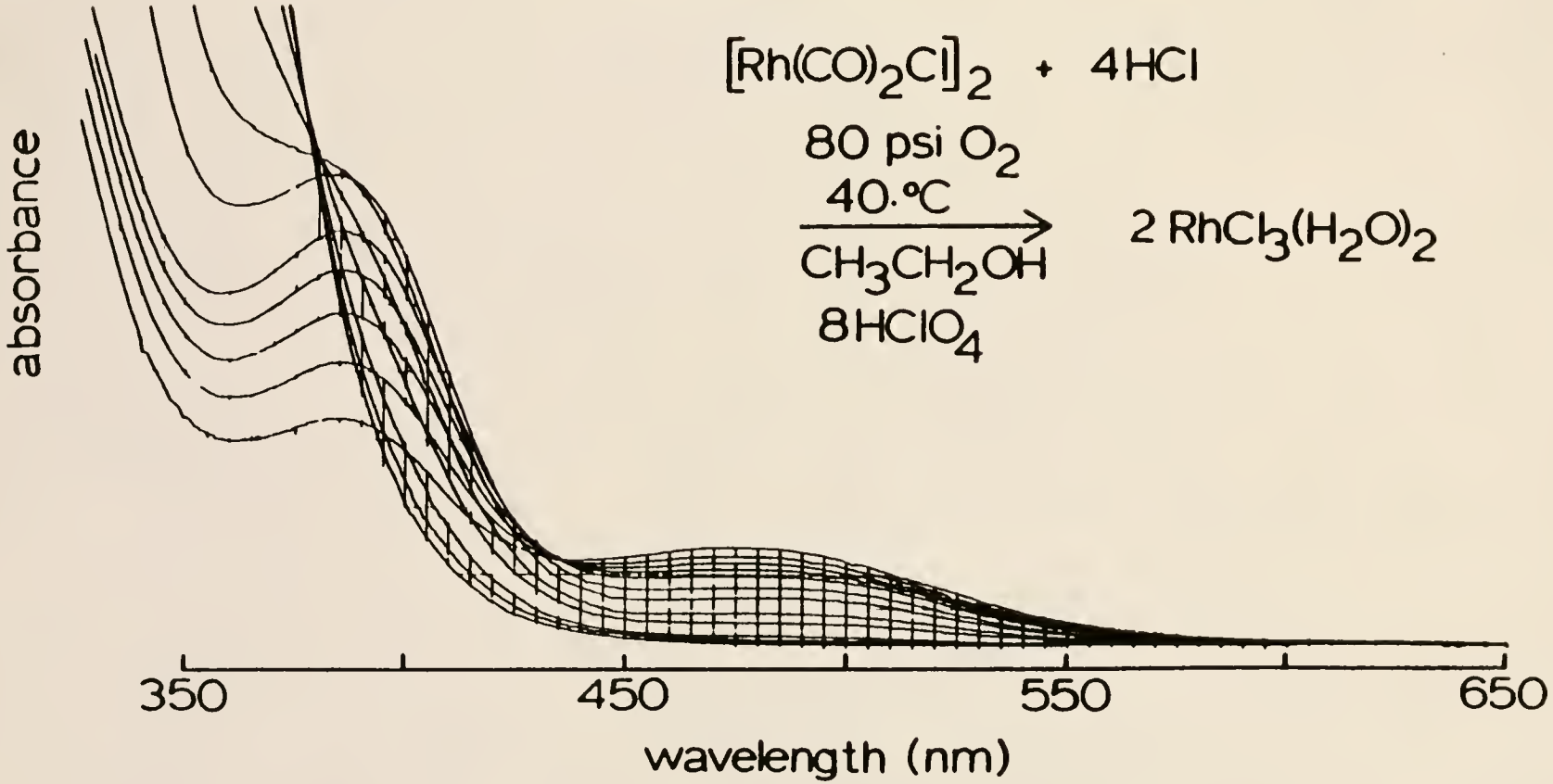

[Rh(CO)2Cl]2 + 4HCl
80 psi O2
40.°C
CH3CH2OH
2 RhCl3(H2O)2
absorbance
350
450
550
650
wavelength (nm)

Figure 5. Series of visible spectra resulting from the O_2 oxidation of $[Rh(CO)_2Cl]_2$ at 40 C in the presence of 8 equivalents $HClO_4$, but otherwise same conditions as used for data presented in Figure 4.



$$[Rh(CO)_2Cl]_2 + 4HCl \xrightarrow[CH_3CH_2OH]{\substack{80\ psi\ O_2 \\ 40.^{\circ}C \\ 8HClO_4}} 2\,RhCl_3(H_2O)_2$$

proposed in two other studies.[32] The rate law in eq. 10 is surprising because it indicates that the initial step or steps in reaction 7 (those including and preceding the rate-determining step) involve a reaction between H^+, O_2, and possibly CH_3CH_2OH, forming an intermediate oxidant which subsequently reacts with $[Rh(CO)_2Cl]_2$.

We investigated the possibility that peroxide could play the role of direct oxidant in reaction 7. This was confirmed by experiments involving the titration of A with HOOH to form C in the absence of dioxygen, monitored by visible spectroscopy (reaction 11, in which S' is solvent).

$$[Rh(CO)_2Cl]_2 + 4HCl + 2HOOH + S' \rightarrow 2RhCl_3(H_2O)_2 \cdot S' + 4CO \qquad (11)$$

Because HOOH slowly disproportionates or is reduced in ethanol, as well as being consumed in a competing side reaction (vide infra), the oxidation of A to C in this solvent goes to only 70% completion. Very significantly the oxidation of A by HOOH proceeds with the formation of the same intermediate [B] as produced with O_2 as oxidant, indicating that reaction 11 and reaction 7 occur through similar mechanisms. The kinetic rate law for reaction 11 was determined by using Fourier transform infrared spectroscopy (FT-IR) to monitor the consumption of A, and is shown in equation 12. Several reports describe the reaction between a

$$-d[A]/dt = k([Rh(CO)_2Cl]_2)[HOOH] \quad (12)$$

metal complex and peroxide to form a coordination compound.[31a-d] The reaction in eq. 11 proceeding as described above would exhibit the rate law shown in eq. 12. On the basis of these arguments and those that follow, we propose that intermediate B results from the coordination of HOOH to $[Rh(CO)_2Cl]_2$. A proton NMR analysis at -70°C showed no evidence for B possessing a hydride ligand. Any hydride species generated from the oxidative addition of HOOH to A apparently are acidic, and fast exchange of all protons with the alcohol solvent is very likely occurring.

The characterization of B was assisted by an FT-IR spectroscopic study of reaction 11. Immediately on adding HOOH to a solution of A and HCl in ethanol, the formation of a complex exhibiting a CO stretching band at 2102 cm^{-1} is observed, and this band increases in intensity at the expense of the bands due to A (at 1995 and 2069 cm^{-1}; Figure 6). The growth and subsequent decay of the CO band at 2102 cm^{-1} was found to correlate directly with the band due to B at 385.nm observed in the electronic absorption spectra. Therefore, intermediate B retains one CO ligand. The assignment of the band at 2102 cm^{-1} to coordinated CO was confirmed by use of ^{13}CO in the experiment.

That B is a hydroperoxo rather than a μ-peroxo complex is evidenced by our ability to substitute tert-butyl hydroperoxide (t-BuOOH) for HOOH in reaction 11 to obtain a

Figure 6. Series of infrared spectra obtained from the HOOH oxidation of $[Rh(CO)_2Cl]_2$ in ethanol. (A) Spectrum of $[Rh(CO)_2Cl]_2$. Reaction was run using 0.84×10^{-3} M $[Rh(CO)_2Cl]_2$. Spectra were recorded at (B) 0.25 hours; (C) 0.55 hours; and (D) 1.83 hours.

A
B
C
D
2500
2000
WAVE NUMBERS

much slower reaction and the formation of an intermediate analogous to B with an electronic absorption band at about 385 nm[33] and an infrared CO stretch at 2099 cm^{-1}, 3 cm^{-1} lower than that found for B with HOOH. Since t-BuOOH is not known to bridge two rhodium species in the μ-peroxo configuration, we suggest that B is not a μ-peroxo complex. Only a limited number of stable hydroperoxide and alkyl peroxide complexes of the platinum metals have been reported[5] (not including those with Schiff base or bio-type ligands), and some of these are capable of oxidizing terminal olefins to 2-ketones.[31a,b] Intermediate B is only formed in the presence of HCl and is not formed on substituting either $HClO_4$ or $N(C_2H_5)_4Cl \cdot H_2O$ for HCl. Thus, both a proton and an additional chloride are required in the formation of the intermediate. We propose that intermediate B is $H_2[Rh(CO)Cl_2^-(OOH)]$, produced as shown in eq. 13. Use of the oxidation

$$[Rh(CO)_2Cl]_2 + 2HOOH + 2HCl \rightarrow 2H_2[Rh(CO)Cl_2(OOH)] + 2CO \quad (13)$$

state formalism to describe these species is potentially misleading. An oxidative addition of HOOH to a Rh(I) complex produces $HRh^{III}OOH$. Deprotonation generates $Rh^{I}OOH^-$. After a number of attempts, we have not been able to observe the O-O stretch between 800 and 900 cm^{-1} expected for a coordinated peroxo group in the infrared spectrum. This is

due to the low concentrations necessary to stabilize this intermediate, the poor window in this region of the infrared spectrum for ethanol solvent, and the hydrogen bonding in this system which would broaden this band. When the intermediate is generated with O_2 and excess O_2 is removed, it spontaneously decomposes to rhodium(III) chloride over several hours. This is consistent with the formulation of this intermediate as $H_2[Rh(CO)Cl_2(OOH)]$, for this species possesses two oxidizing equivalents in the peroxo (or hydroperoxo) ligand.

Intermediate B is not formed in the absence of HCl in reaction 11, but the reaction in eq. 14 occurs under argon in ethanol solvent,

$$[Rh(CO)_2Cl]_2 + HOOH \xrightarrow{Ar} 2CO_2 + D \qquad (14)$$

producing free CO_2 from the oxidation of a CO ligand and a very deep brown rhodium(I) complex (D) exhibiting a broad CO stretching band at 2048 cm^{-1}. Thus, $[Rh(CO)_2Cl]_2$ could be reformed from D by exposure to a CO atmosphere, and the production of CO_2 from the CO oxidation by HOOH is catalytic in A in a CO atmosphere. This reaction has been previously reported in benzene,[34] where D precipitates. It is reported[34] that redissolving this solid in ethanol and exposing it to CO leads to the formation of a rhodium(I) carbonyl complex with a spectrum <u>similar</u> to A. Reforming $[Rh(CO)_2Cl]_2$ from D under CO is significant because it

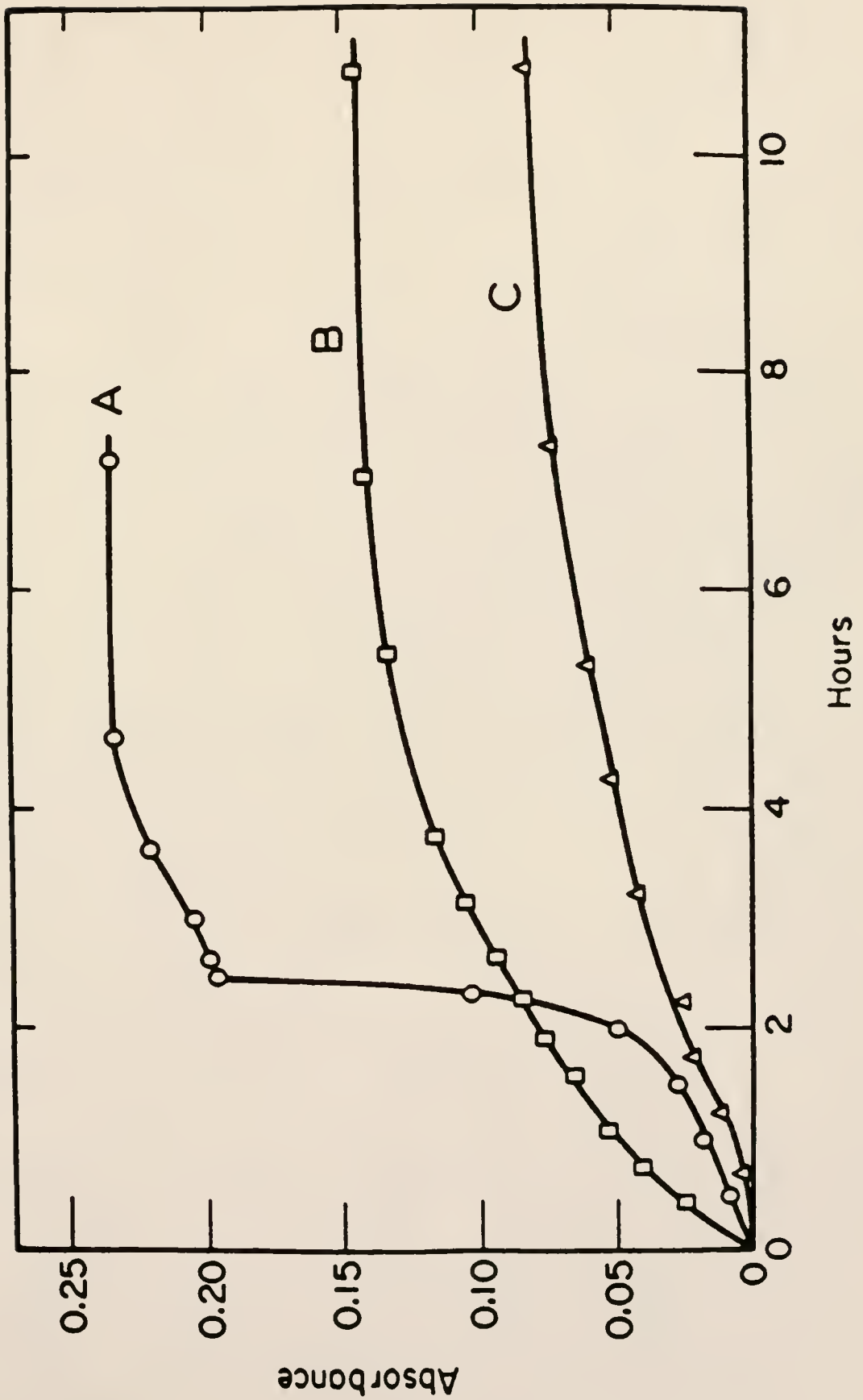
indicates that D is a rhodium(I) complex and that the irreversible oxidation of rhodium(I) to rhodium(III) by HOOH in ethanol is slow relative to the oxidation of the CO ligands to CO_2 (which takes several hours). These results further suggest that in the presence of HCl the reaction between A and HOOH produces the relatively stable rhodium(I) hydroperoxo coordination complex B as an intermediate. In the presence of HCl reaction 3 is faster than reaction 14, and the majority of HOOH is consumed to form B rather than CO_2 and D. That reaction 14 does occur to a small extent in the presence of HCl can be seen in Figure 6, in which the band at 2334 cm^{-1} due to CO_2 is evident. This competing reaction accounts, at least in part, for the incompleteness noted for the titration of A with HOOH in reaction 11.

The stabilization of B by excess Bronsted acid, evidenced by a comparison of the electronic absorption spectra in Figures 3 and 4, can be explained by considering the deprotonation of the RhOOH group as the initiation step for the reaction of B to form C. A further investigation of the decomposition characteristics of B also proved to be useful. Upon isolation of a mixture of B and C by quick evaporation of a dilute solution to dryness under vacuum, B decomposes within a minute to a wet solid. An infrared spectrum of this product revealed a large concentration of water in addition to a high-energy CO stretching band at 2132 cm^{-1} (shifted from 2102 cm^{-1} for B). These are the results expected from the fast, autocatalytic decomposition

of a hydroperoxo complex. The reduction of the hydroperoxo ligand by Rh(I) will produce H_2O and a rhodium(III) carbonyl. This oxidized metal complex will be much poorer at back-bonding into the CO than was the rhodium(I) in B, and therefore its stretching frequency would be shifted nearer to that for free CO (at 2143 cm^{-1}). Finally, in Figure 7 are presented data which illustrate the effect of increasing the rhodium concentration on the rate of decomposition of the intermediate. This rate was measured by monitoring the electronic absorbance for C at 480 nm. It is evident that at a threshold concentration in A between 0.98×10^{-1} M and 1.47×10^{-3} M, the reaction of B to form C becomes autocatalytic in character. At 0.98×10^{-3} and 0.68×10^{-3} M this reaction follows a much more regular course. These results indicate that a free radical decomposition of intermediate B is a sustained process only above the threshold rhodium concentration. Indeed, the electronic absorption spectra indicate that at much high concentrations, reaction 7 is less specific to the exclusive formation of C. In this case the band at 480 nm for C is present only as a plateau due to the absorbance of a secondary rhodium(III) product which absorbs at lower wavelengths.

The characterization of intermediate B and the rate law in eq. 10 have an importance not yet discussed. They indicate that in reaction 7, hydroperoxide is initially formed from the Bronsted acid catalyzed reduction by dioxygen by ethanol or isopropyl alcohol solvents (eq. 15). The

Figure 7. Demonstration of the autocatalytic formation of $RhCl_3(H_2O)_2CH_3CH_2OH$ above the threshold concentration (profile A). Concentrations in $[Rh(CO)_2Cl]_2$ are for (A) 1.47×10^{-3} M; (B) 0.98×10^{-3} M; and (C) 0.68×10^{-3} M.


A
B
C
0.25
0.20
0.15
0.10
0.05
0
0
2
4
6
8
10
Absorbance
Hours

$$CH_3CHROH + O_2 \rightarrow CH_3CRO + HOOH \qquad (15)$$
$$R \equiv CH_3 \text{ or } H$$

oxidation of primary and secondary alcohols to aldehydes and ketones using dioxygen has been known for some time.[35,36] These oxidations may be divided into two categories: (1) free radical initiated reactions, using asoisobutyronitrile (AIBN) for example, and (2) metal-catalyzed oxidations. The principal difference is that oxidations of the first type may produce HOOH stoichiometrically[9] (eq. 15) as long as precautions are taken to stabilize hydrogen peroxide while oxidations of the second type produce water[10] (eq. 8), because the metals which catalyze HOOH formation also catalyze decomposition of hydroperoxides to H_2O and O_2 very efficiently. Thus, there is literature precedence supporting our proposal that HOOH is produced (albeit inefficiently) with a Bronsted acid as a catalyst.[37]

Under our reaction conditions the HOOH concentration reaches a very low steady-state value, accounting for the slow initial rate of oxidation of A (eq. 7) and our inability to detect HOOH by iodometric techniques in acidic ethanol solutions under O_2. However, we have obtained indirect evidence of HOOH production in two series of experiments in which H^+, Cu(II) and Rh(III) were checked for their ability to (1) speed up the oxidation of A (eq. 7) by producing HOOH

catalytically from the alcohol reduction of O_2 and (2) catalyze the oxidation of isopropyl alcohol (eq. 8) as measured by acetone production. For the investigation of the effect of these three reagents on the rate of oxidation of A (eq. 7), we worked at 1 atm rather than at 80 psi of O_2 (5.4 atm) because the reaction is much slower at this reduced pressure. As shown in experiment D in Table I, no final product is observed at 480 nm in the electronic absorption spectra in the absence of $HClO_4$, Cu(II) or Rh(III) after 1 hour, and the reaction take 36 hours to come to completion. In contrast, the addition of 0.1 equiv of Cu(II) or Rh(III) at the beginning of the oxidation of A (eq. 7) results in a much faster reaction, with Cu(II) being most efficient (experiments A and B). Doubling the acid concentration also speeds up the reaction but to a much lesser extent (experiment C). From these data it appears Cu(II) and Rh(III), and to a much lesser extent H^+, catalyze the production of HOOH from ethanol reduction of O_2, and this causes the increased rates observed for the oxidation of A (eq. 7) in their presence.

Substantiation of this was found from our investigation of the effectiveness of Cu(II), Ru(III) and H^+ in catalyzing the oxidation of isopropyl alcohol (eq. 8). Their effectiveness at the beginning of this reaction follows the order Cu(II) $\sim$ Rh(III) $>>$ H^+, with rhodium resulting in 19 turnovers (acetone/rhodium) in 25 h and H^+ producing only a trace amount of acetone.[38] The consumption of dioxygen when

Rh(III) was used for reaction 8 was also followed on a gas burette for several hours and is linear over that time, indicating this catalyst is not slowly rendered inactive. It is reasonable to suggest that HOOH, or peroxo metal complexes, are formed as intermediates in reaction 8 and that the efficient catalysis of this oxidation is evidence of the ability of a reagent to catalyze the production of peroxide from the alcohol reduction of O_2. Because both Cu(II) and Rh(III) are efficient hydroperoxide decomposition catalysts, the HOOH is produced at a very low steady-state concentration and may in fact never leave the coordination sphere of the catalysts.

Experiment E in Table I demonstrates unequivocably that an intermediate oxidant (HOOH) is formed in the presence of only HCl, $HClO_4$, ethanol, and O_2. This has been labled an "incubation" experiment because it involved stirring 3.2×10^{-3} M each of HCl and $HClO_4$ in ethanol under 1 atm of O_2 at $40^{\circ}C$ for 48 hours, followed by the addition of the $[Rh(CO)_2Cl]_2$ to initiate reaction 7. In this case upon adding A no induction period was observed and the reaction was complete in only 7 hours compared to the 36 hours necessary when mixing all reagents from the start. In agreement with the rate law in eq. 10, this further indicates that the first step in the oxidation of A involves the production of HOOH from H^+, O_2 and CH_3CH_2OH and that hydroperoxide is the reagent directly responsible for the oxidation of $[Rh(CO)_2$-

Table I. Oxidation of $[Rh(CO)_2Cl]_2$.

Experiment	Catalyst[a]	Relative Absorbance for Complex C at 480 nm at 1.0 h	Time for Completion of Reaction 7
A	0.15 mM Cu(II)	14	4
B	0.17 mM Rh(III)	3	10
C	4.2 mM $HClO_4$	0[b]	14
D	None	0	36
E	"Incubation"[c]	1	7

[a]These reactions were run at 40°C and 1 atm of O_2, using 0.80×10^{-3} M $[Rh(CO)_2Cl]_2$, 3.2×10^{-3} M HCl, and 22.5 mL of ethanol as solvent, in addition to the catalyst listed.

[b]No final product II could be detected after 1.0 h.

[c]This run involved stirring 3.2×10^{-3} M HCl and 3.2×10^{-3} M $HClO_4$ in ethanol at 40°C and 1 atm of O_2 for 48 h, followed by the addition of $[Rh(CO)_2Cl]_2$ to a 0.90×10^{-3} M concentration.

$Cl]_2$ to rhodium(III) chloride in ethanol via a hydroperoxo-rhodium complex intermediate. Our proposed mechanism for this oxidation is shown in Scheme I and is substantiated by all of the preceding evidence and arguments.

Scheme I

$$CH_3CHROH + O_2 \rightleftharpoons CH_3CRO + HOOH \qquad (a)$$

$$[Rh(CO)_2Cl]_2 + 2HCl + 2HOOH \rightleftharpoons 2[Rh(CO)Cl_2(OOH)]^{2-} + 4H^+ + 2CO \qquad (b)$$

$$[Rh(CO)Cl_2(OOH)]^{2-} + 2H^+ \rightleftharpoons [Rh(CO)Cl_2(OO)]^{3-} + 3H^+ \qquad (c)$$

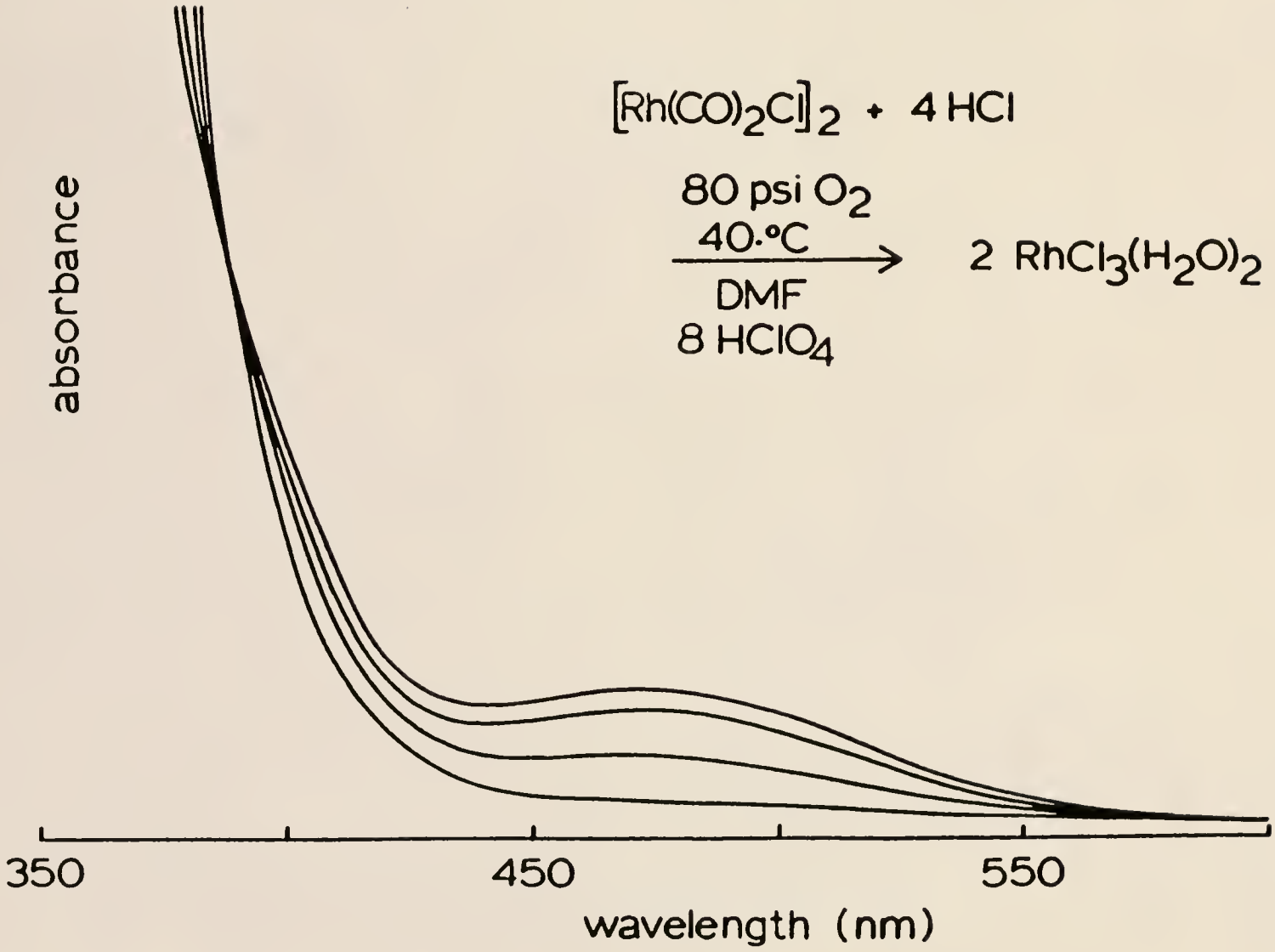
$$[Rh(CO)Cl_2(OO)]^{3-} + 4H^+ + Cl^- + CH_3CHROH \rightarrow RhCl_3(H_2O)_2 \cdot CH_3CHROH \qquad (d)$$

An intermediate analogous to B is not produced when $[Rh(C_8H_{14})_2Cl]_2$ is used instead of $[Rh(CO)_2Cl]_2$ as the rhodium(I) starting material in a reaction similar to that in eq. 7. In this case the reaction to form rhodium(III) chloride is complete in only 40 min (compared to 12 hours under identical conditions with A), and no evidence for intermediates is found in the electronic absorption spectra. In contrast, $[Rh(P(tolyl)_3)(CO)Cl]_2$ is not oxidized to rhodium(III) chloride even after 48 hours.

Since Scheme I requires solvent reducing equivalents to produce HOOH and subsequently $[Rh(CO)Cl_2(OOH)]$ from O_2, any solvent capable of this O_2 reaction could lead to the oxidation of A by this mechanism. Indeed, we have found that methanol, ethanol, isopropyl alcohol, and to a lesser extent tetrahydrofuran (THF), all produce B as an intermediate in the oxidation of A by O_2. In THF this could appear through the intermediacy of THF hydroperoxide, produced from the abstraction of an α-hydrogen atom by O_2 and a subsequent radical coupling reaction. The THF-hydroperoxide may react with $[Rh(CO)_2Cl]_2$ as do both HOOH and t-BuOOH. In contrast, use of the typically nonreducing solvents tert-butyl alcohol, acetone,[39] and N,N-dimethylformamide (DMF) does result in oxidation of $[Rh(CO)_2Cl]_2$ without forming B as a stable intermediate. In tert-butyl alcohol and acetone the reaction is very fast, finishing in 40 min under conditions for which it takes 10 hours for completion in ethanol. In DMF the reaction is much slower (also taking 10 hours) and was monitored by electronic absorption spectroscopy. In this solvent only one isosbestic point is observed (at 390 nm) due to the production of rhodium(III) trichloride from the oxidation of $[Rh(CO)_2Cl]_2$ without the formation of any stable intermediates (Figure 8).

It is interesting that the oxidation of A (eq. 7) proceeds through the coordination of HOOH to $[Rh(CO)_2Cl]_2$ in primary and secondary alcohol solvents rather than proceeding

Figure 8. Series of visible spectra for the O_2 oxidation of $[Rh(CO)_2Cl]_2$ to rhodium(III) trichloride in DMF as solvent.


[Rh(CO)2Cl]2 + 4 HCl
80 psi O2
40.°C
DMF
8 HClO4
2 RhCl3(H2O)2
absorbance
350
450
550
wavelength (nm)

by the alternative mechanism that seems to occur in tert-butyl alcohol, acetone and DMF. When THF is used as solvent the reaction is much faster and only poor resolution of the electronic absorption band due to B is observed. This is due to a lower concentration of B relative to that found in the alcohols, and possibly a low energy absorption band.[40] In THF it may be that both mechanisms are functioning, which would explain the low concentration of B observed. It is important to note that we cannot rule out the alternate mechanism occurring in methanol, ethanol, and isopropyl alcohol solvents to a small degree. However, it is evident from the magnitude of the bands due to B in the electronic absorption and infrared spectra, as well as data from the kinetic rate law in eq. 10, that Scheme I involving the coordination of HOOH to $[Rh(CO)_2Cl]_2$ is dominant in primary and secondary alcohols.

Conclusion

It is usually necessary to include bio-type or Schiff-base ligands in order to prepare a hydroperoxide complex, which makes the characterization of B as $H_2[Rh(CO)Cl_2(OOH)]$ noteworthy. The CO ligand seems to be responsible for at least some amount of the stability of this complex. It is this stability which does not lead to the characterization of the complex as an intermediate in the catalytic oxidation of 1-hexene to 2-hexanone. Complex B

appears to have only slight (if any) reactivity as a catalyst for 1-hexene oxidation. This result is not unexpected when a comparison is made between the rhodium(III) active catalyst and the rhodium(I) hydroperoxo complex, B.

The fact that primary and secondary alcohols can form low concentrations of HOOH from the reduction of O_2 may also have several implications. Other metal complexes may have to be included with H^+, Cu(II) and Rh(III) as catalysts for the alcohol reduction of O_2 to HOOH. Systems which require long term exposure to alcohol and O_2 may find the low concentrations of HOOH produced to be quite significant. Substrate oxidations of O_2 via HOOH formation may also be more prevalent than now realized.

Further results have shown HOOH and t-BuOOH to both be effective reagents in the $RhCl_3 \cdot 3H_2O$ catalyzed oxidation of 1-hexene to exclusively 2-hexanone in the absence of O_2. The results are the same whether the solvent is ethanol or tert-butyl alcohol (which has no reducing equivalents). These facts provide still further justification for the characterization of the active catalyst for reaction 1 as a rhodium(III) chloride complex.

Experimental Section

All solvents and reagents were of reagent grade and used without further purification. Literature methods were used to prepare $[Rh(CO)_2Cl]_2$.[41] Hydrogen peroxide and tert-

butyl peroxide were used as 30% and 70% aqueous solutions, respectively, and were standardized iodometrically. The acids HCl, H_2SO_4, and $HClO_4$ were used as their concentrated aqueous solutions.

Infrared spectra were recorded on a Nicolet 7000 Series Fourier transform infrared spectrometer. GLC spectra were obtained with a Varian Model 940 FID instrument using a 3-m,1/16 in. i.d. copper column packed with Chromasorb P supported diethylene glycol adipate. For the detection of acetone a column temperature of 60°C was employed, and the measurement of 2-hexanone was quantitated by using 2-heptanone as an internal standard. The electronic absorption spectra were recorded on a Cary 14, and all samples were run in air at ambient temperature and pressures. Care was taken to verify that the intermediates monitored by this technique were stable over the course of the measurements. The molecular weight of C was determined in methanol by vapor pressure osmometry.

Catalytic Oxidations of 1-Hexene

All catalytic 1-hexene oxidations were run in 250-mL Parr pressure bottles equipped with bras Swagelok pressure heads. These were constructed to allow purging with O_2, as well as sampling of the solution under reaction conditions during the course of the reactions. 2-Hexanone production was measured by GLC.

A typical catalytic reaction was run as follows: to a 250-mL Parr bottle were added 0.074 mmol of $[Rh(CO)_2S'_n]BF_4$

(prepared as earlier reported[2] and used immediately), 0.0171.g of $Cu(NO_3)_2 \cdot 2.5H_2$ (0.074 mmol), 0.0219 g of NaCl (0.375 mmol for the case in which 5:1 mole ratio chloride/ rhodium was desired), 0.41 mL of 0.36 M H_2SO_4 (0.148 mmol as an ethanol solution prepared from aqueous concentrated H_2SO_4), 0.568 mmol of 2-heptanone, 45 mL of absolute ethanol, and 15 mL of 1-hexene (purged through alumina to remove peroxides). This mixture was purged 5 times with 60 psi of O_2, set to 40 psi of O_2, and the reaction initiated by placing in a 70°C oil bath.

Preparation of $RhCl_3(H_2O)_2CH_3CH_2OH$ (II)

Compound C was prepared for characterization studies most easily under 40 psi of O_2 at 70°C by mixing 0.0514 g of $[Rh(CO)_2Cl]_2$ (0.132 mmol), 1.10 mL of 0.48 M HCl (in ethanol, 0.528 mmol), and 15 mL of ethanol. This produced a bright orange solution after a reaction overnight, from which C was isolated by rotovapping to dryness and drying in vacuo. The M_r for $H_4O_2Cl_3Rh$ calcd. 245; found, 226. Anal. Calcd for $C_2H_{10}O_3Cl_3Rh$: C, 8.24; H, 3.46; Cl, 36.50. Found: C, 8.41; H, 2.69; Cl, 37.17.

Determination of Acetone Production

In Presence of 1-Hexene. The measurement of acetone produced in the initial stage of the Rh/Cu-catalyzed oxidation of 1-hexene with isopropyl alcohol as solvent was made by GLC as follows: To a 50-mL round-bottom flask were

added to 0.159 g of $RhCl_3 \cdot 3H_2O$ (0.605 mmol), 0.137 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.589 mmol), and stir bar. This was purged 20 min with O_2 at 40°C and 30 mL of an O_2-purged, 9/1 (v/v) solution of isopropyl alcohol/1-hexene added to initiate the reaction. GLC's were recorded after 4, 8, 17, 25 and 40 min. The amount of acetone produced was determined by comparison of peak heights with standards at the same time under identical conditions. When this 1:1 Cu/Rh ratio was used, 0.5 mol of acetone was formed per mole or rhodium in the first 4-8 min. No further production was observed. When a 2:1 Cu/Rh mole ratio was used, continuous, catalytic production of acetone was observed.

In Absence of 1-Hexene. The catalytic production of acetone from the O_2 oxidation of isopropyl alcohol was observed when 1-hexene was excluded from the solutions. Both $RhCl_3 \cdot 3H_2O$ (0.140 mmol) and a stir bar were placed in a 15-mL round-bottom flask and purged 20 min with O_2 at 40°C. Into this was syringed 7 mL of isopropyl alcohol, purged itself with O_2 at 40°C, to initiate the reaction. Acetone production was measured as described above.

Titration of $[Rh(CO)_2Cl]_2$ with HOOH

Because the reaction of HOOH with $Rh(CO)_2Cl_2$ (A) is quite slow in ethanol, it was run at 40°C. The visible spectrum of the intermediate, $H_2[Rh(CO)Cl_2(OOH)]$ (B), is not clearly observed by first adding 1.0 equiv of HOOH, followed an hour later by 0.5 equiv. The first addition causes the

reaction of much of the starting material A (which overlaps the band at 385 nm), so that after the second addition the band due to C at 385 nm is easily observable in the electronic absorption spectrum. Intermediate B is easily detected in the oxidation of A by HOOH by using FT-IR. Since there is no overlap of the carbonyl bands of A and B, the intermediate is detected in the first addition of HOOH. Immediately after use HOOH was diluted in ethanol. Aqueous dilution causes the addition of too much H_2O, which retards the reaction considerably.

CHAPTER III
ENHANCED SITE ISOLATION ON SILICA GEL AND IMPROVED LIFETIMES OF SITE ISOLATED CATALYSTS

Introduction

Functionalized polymers have been increasingly employed to support transition metal complexes as catalysts in recent years. There have been several reviews in the literature involving both organic supports[42-47] and inorganic solids.[48-50] The system of interest here involves functionalized supports which usually contain molecularly definable species. Such systems are largely in the minority, because they do not include either (1) the deposition of metals or metal oxides by the oxidation or reduction of metal complexes, or (2) the intercalation of metals in unfunctionalized inorganic oxides.

The lack of physical methods which can routinely provide identification of surface supported metal complexes hinders the development of new catalytic systems. As a result, attempts to prepare supported catalysts are often based upon known homogeneous systems. The approaches for

attaching metal complexes is often guided by the ligand system of the homogeneous catalyst. The methods which have been utilized include ligand exchange or substitution of the metal complex to the support,[51,52] addition to unsaturated metal complexes,[53,54] and ionic attachment.[55,56]

Immobilization of metal complexes on solid supports can provide advantages over both homogeneous and heterogeneous catalysts. Included in these are (1) the ease of separating solid catalyst from the reaction mixture, which encourages the use of flow reactors, (2) the ability to greatly increase dispersion of the metal on the surface, allowing the use of less metal (and finances), and (3) reduced contact with the reaction vessel leading to reduced corrosion. This potential for gaining the advantages of both homogeneous and heterogeneous catalysts has many industrial applications which are being investigated.

Following below is a brief discussion of the general properties of the inorganic solid, silica gel, which is used as a catalytic support in the research presented in this chapter.

Silica gel has a surface which is very irregular consisting of hydroxyl and silicon bridging oxide groups. It is quite rigid and contains many channels throughout its structure and only the silica gel surface may be functionalized. Silica gel samples which vary widely in surface area are available. Several characteristics of silica gel make it potentially preferable to organic polymers as a support for

metal complexes. The rigidity of its silicon oxide tetrahedra is often an advantage for immobilizing and site isolating catalytic centers. The stability of silica gel at higher temperatures than organic polymers may also be important. Finally, the large number of organosilanes which are becoming commercially available and the mild conditions under which functionalization is achieved makes the number of possible silica supported moieties quite large.

As mentioned above, organosilanes are employed to functionalize the surface of silica gel. It has been reported that the reaction proceeds by hydrolysis, hydrogen bonding and final bond formation as shown in Figure 9 as reactions a-c.[57] The symbol [SG]-OH is used to represent unfunctionalied silica gel.

An investigation of the nature of the binding of organosilanes to the silica surface was recently reported.[58] Before this study was reported, it was generally believed that three bonds from the silane to the silica suface were formed. However, in this report Waddell et al. state that most commonly only one bond is formed from silane to silica, while the formation of two bonds is possible, and tridentate bonding seems unlikely due to steric limitations.

Another important characteristic of polymer bound metals is the ability to achieve site isolation of the metal complex on the polymer surface. Solid supports can function to avoid molecular aggregation and prevent the formation of multinuclear complexes or clusters. This usually requires

Figure 9. General reaction scheme for the functionalization of the surface of silica gel, [SG]-OH.

$$R_3SiCl + H_2O \rightarrow R_3Si(OH) + HCl \quad (a)$$

$$R_3Si(OH) + [SG]\text{-}OH \rightarrow [SG]\text{-}O\text{---}H\text{---}OH(Si)R_3 \quad (b)$$

$$[SG]\text{-}O\text{--}H\text{---}OH(Si)R_3 \rightarrow [SG]\text{-}O(Si)R_3 + H_2O \quad (c)$$

dilution of active sites on the surface in order to minimize contact of supported metal complexes, although another method has been successful at achieving site isolation (vide infra). Most of the work reported in supporting metal catalysts has employed very large loadings of the polymeric surface with the desired functional group and metal complex. In these cases elemental analyses can often be utilized, which is advantageous since there are so few physical methods available. However, this has led to a lack of research on systems with definite site isolation of active species, or possible improvement of existing catalysts by the establishment of site isolation. Rigid, non-flexible polymeric supports such as silica gel are usually required when attempts to obtain site isolation of a supported species are undertaken.

There are several reports of functionalized silica gel being used to achieve site isolation, and perhaps other examples from industrial laboratories which have not reached any available literature. Among the reported examples are a bound imidazole iron tetraphenylporphyrin which is used to reversibly bind dioxygen,[59] and cyclopentadiene groups supported on silica gel which form stable mononuclear iron and cobalt carbonyl complexes.[60]

Results and Discussion

Polymer Support of the Catalyst

The oxidation of terminal olefins to 2-ketones catalyzed by rhodium and copper was discussed in some detail in the previous chapter in relation to its homogeneous mechanisms. Here will be described an investigation to increase that catalyst's relatively short lifetime by attempting to provide an ideal supported environment for the catalytic species. Prevention of the suspected deactivating oxidative aggregation of the rhodium catalyst was the rationale for this approach.

Required of a solid support is a solvent independent rigidity which could improve prospects for obtaining site isolation. Silica gel, unlike organic polymers such as polystyrene, meets these requirements. Initial attempts at using an organosulfide ligand on silica gel to bind the rhodium/copper cocatalysts were successful.[61] Goals of improving the activity and lifetimes of supported catalysts while gaining a detailed knowledge of the silica surface precipitated the research described in this chapter.

Silica gel supported organosulfide samples (abbreviated [SG]-SH) were synthesized using (3-mercaptopropyl)trimethoxysilane [$(CH_3O)_3Si(CH_2CH_2CH_2SH)$] reacted with plain silica gel. A simple model was used to help gain insight into the surface coverage on the silica gel. Approximating the

silicon-oxygen bond distance as two Angstroms and assuming tetrahedral coordination around silicon, then the distance between oxygen atoms of the surface silanol groups is 6.5 Å. In order to obtain an upper limit it is assumed that a flat surface exists and that all of the surface groups are silanols (-SiOH). Since the Davison Grade 62 silica gel employed has a surface area of 340 m^2/g [SG], then there is approximately one surface hydroxyl group per 4.3 x 10^{-9} m^2 of surface. Thus, it can be calculated that as an upper limit there are about one mmol of surface silanol groups per gram [SG]. With this value it can be calculated that the [SG]-SH samples prepared contain approximately 1/40, 1/20, 1/10 and 1/5 mmol sulfide/mmol surface Si (S/Si) which correspond to 0.025, 0.5, 0.10 and 0.20 mmol S/g[SG]. The number of mmol S/g[SG] was determined by electronic absorption for all samples as described in the experimental section and is independent of the model and calculations discussed above. The values for the number of mmol S/g[SG] varied only a small amount between preparations of functionalized silica gels. It was these experimental values which were employed to determine the amount of silica gel necessary for each catalytic oxidation. The general labels used to represent [SG]-SH samples of different sulfide loadings are shown in Table II.

Also worthy of consideration is the relatively large potential surface area over which the supported rhodium complex may cover due to its attachment to a chain of six

Table II. Representations used to designate [SG]-SH samples of varying sulfide concentrations.

SH Loadings on [SG] Surface		
0.025 mmole S/g [SG]	→	1 surface -SH/ 40 surface -SiOH
0.05 mmole S/g [SG]	→	1S/20Si
0.10 mmole S/g [SG]	→	1S/10Si
0.20 mmole S/g [SG]	→	1S/ 5Si

atoms. Despite not being linear, this chain still allows a 380 square Angstrom area over which each rhodium may migrate. This number, along with the surface Si concentration, allows the calculation that the silica surface must have a concentration less than 1 S/g surface Si in order for site isolation of the rhodium to exist. This is a convenient number to which properties of actual [SG]-SH samples may be compared.

Preparation of supported rhodium complexes on silica gel was achieved by utilizing freshly generated $[Rh(CO)_2S'_n]BF_4$ (S' = solvent) in ethanol[62] or tetrahydrofuran (THF) as shown in reaction 16.

$$[Rh(CO)_2Cl]_2 + 2AgBF_4 \rightarrow 2[Rh(CO)_2S'_n]BF_4 + 2AgCl \qquad (16)$$

This rhodium cation readily binds to [SG]-SH samples at room temperature producing silica gels varying from bright yellow to red-orange as the concentration of surface sulfide is increased.

The carbonyl ligands in the rhodium complex bound to the silica gel allows the use of infrared spectroscopy to investigate the functionalized surface. In these studies freshly prepared $[Rh(CO)_2S'_n]BF_4$ (S' = solvent) was reacted with [SG]-SH sample under nitrogen and an infrared spectrum quickly taken. The supported rhodium complex produced on many dilute functionalized gels (e.g., 1S/40Si) yields a two-band infrared spectrum (2055 and 2005 cm^{-1}) characteristic

of $[SG]SRh(CO)_2S'_n$ (S' = solvent). More concentrated [SG]-SH samples (e.g., 1S/5Si) treated identically produce three-band spectra (2075(m), 2055(s), and 2005(s) cm^{-1}) indicative[52] of a supported dimer, $([SG]-S)_2Rh_2(CO)_4$. These different surface species are represented in Figure 10. It seems very evident that concentration of surface sulfide groups past a certain point removes site isolation and permits supported rhodium dimerization. These trends and their implications will be discussed further in later sections.

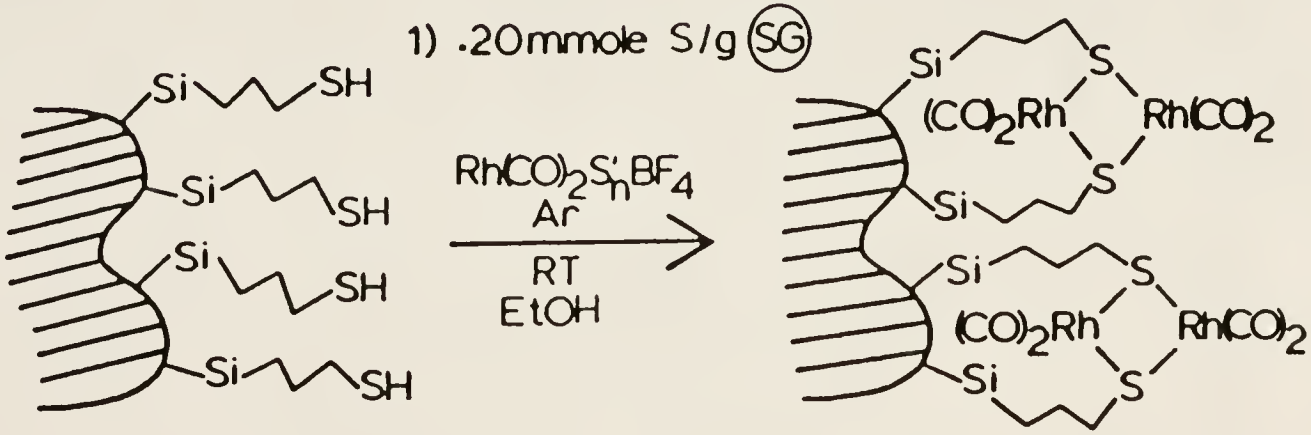
Catalytic Oxidations of 1-Hexene by Supported Complexes

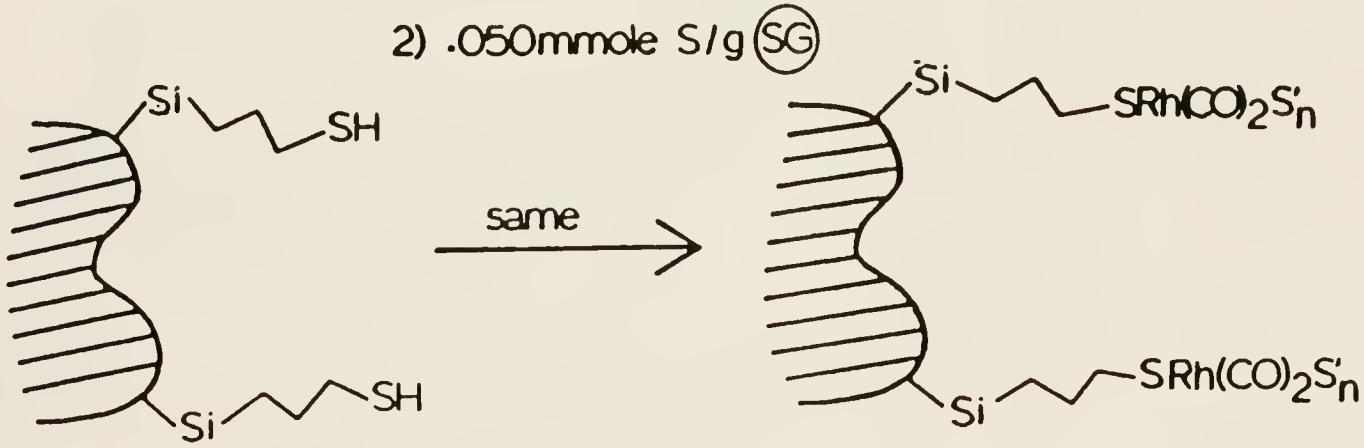
Silica gel organosulfide supports ([SG]-SH) as described previously were used to immobilize rhodium and copper in order to investigate in detail the heterogeneous catalytic oxidation of 1-hexene to 2-hexanone (reaction 17).

$$2CH_2{=}CH(CH_2)_3CH_3 + O_2 \rightarrow 2CH_3\overset{\overset{O}{\|}}{C}(CH_2)_3CH_3 \qquad (17)$$

Electronic absorption (as described in the Experimental Section) was used to quantify the amount of sulfide in each silica gel sample. The amount of sulfide present determined the quantity of [SG]-SH used as a support in each catalytic oxidation. Each oxidation to be discussed employs 0.074 mmol of both $[Rh(CO)_2S'_n]BF_4$ (S' = solvent) and $Cu(NO_3)_2 \cdot 3H_2O$. The quantity of [SG]-SH which provides 0.16 mmol of sulfide

Figure 10. Representation of the different supported rhodium complexes obtained with (1) 1S/5Si-[SG]-SH and (2) site-isolated 1S/20Si-[SG]-SH.


1) .20mmole S/g SG
Si
SH
Si
SH
Si
SH
Si
SH
Rh(CO)2S'nBF4
Ar
RT
EtOH
Si
S
(CO)2Rh
Rh(CO)2
S
Si
Si
S
(CO)2Rh
Rh(CO)2
Si
S


2) .050mmole S/g SG
Si
SH
Si
SH
same
Si
SRh(CO)2S'n
Si
SRh(CO)2S'n

sites (a 10% excess) is used in each oxidation. Also added to each reaction were 2 equivalents of $HClO_4$ (based on moles of rhodium), 15 equivalents of 2-haptanone internal standard, 45 mL absolute ethanol solvent and 15 mL 1-hexene substrate. An apparatus of 250 mL Parr pressure bottles was used to conduct the experiments along with a pressure head which allowed the removing of aliquots of the reaction mixture under reaction conditions. Reactions were initiated by purging the pressure bottle containing all components of the reaction five times with 60 psi O_2, setting the pressure to 40 psi O_2 and placing the apparatus in a 70°C oil bath. The $HClO_4$ was used because Mimoun found a Bronsted acid to be necessary when using rhodium(I) in his homogeneous investigation, and it is given a role in his proposed mechanism. Gas-liquid chromatography (GLC) was employed to follow the catalytic oxidations. A calibration curve of 2-hexanone product versus 2-heptanone standard was used to calculate 2-hexanone production in millimoles.

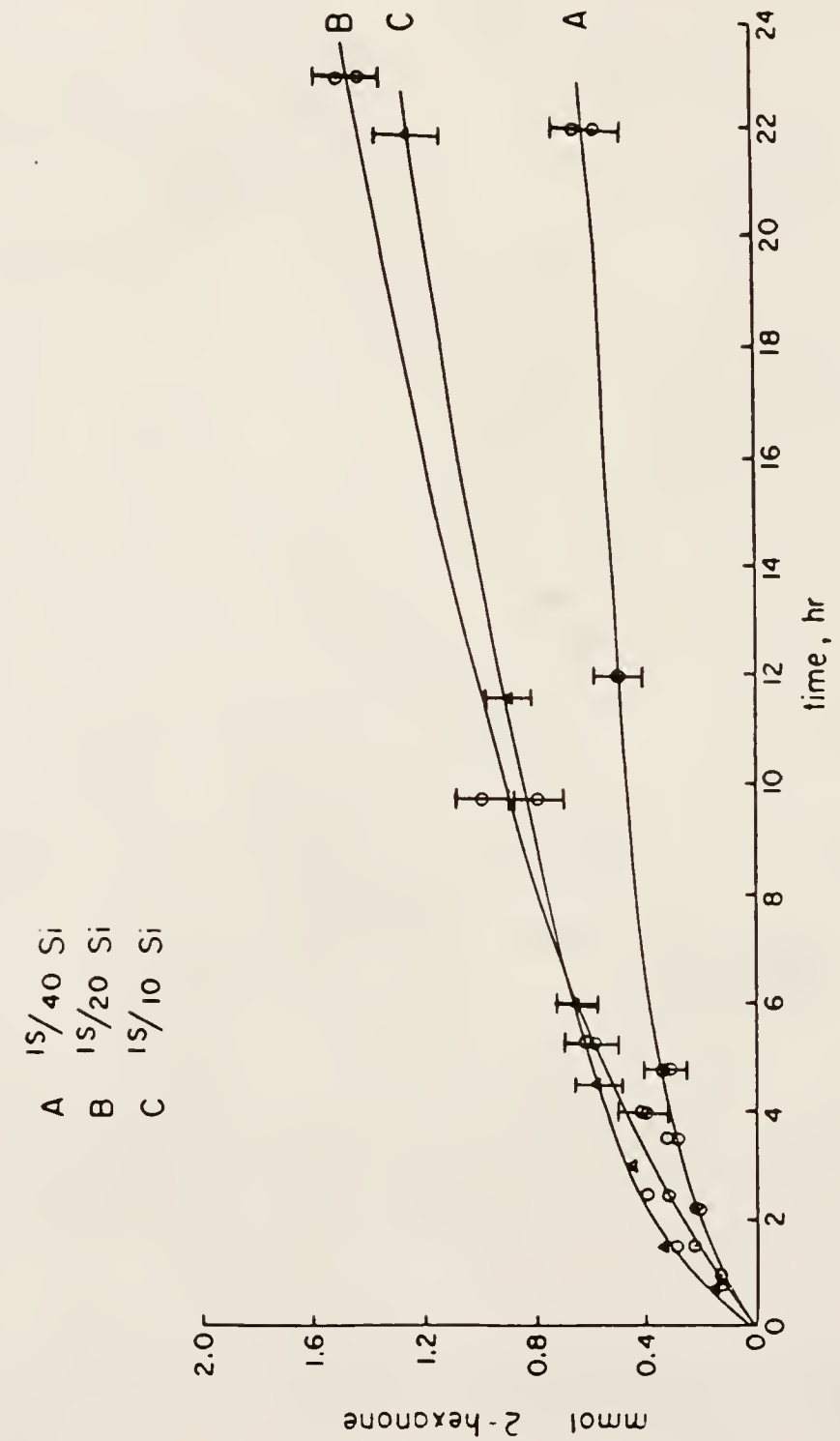
In preparing [SG]-SH supports, if it is assumed that all of the added $(CH_3O)_3SiCH_2CH_2CH_2SH$ reacts completely, one obtained values for [SG]-SH of 0.025, 0.050, 0.100 mmol S/g[SG] corresponding to 1S/40Si, 1S/ 20Si, and 1S/10Si, respectively. The analysis for sulfide (using a rhodium complex and electronic absorption as in the Experimental Section) for a series of [SG]-SH samples produces values of 0.020, 0.041, and 0.076 mmol S/g[SG]. These values are reasonably close to those expected for complete reaction and

also have relative ratios to one another very similar to those which assume complete reaction. Again, it is the experimental values for sulfide content which are used in determining the quantity of [SG]-SH necessary for each catalytic oxidation.

Results of the heterogeneous catalytic oxidation of 1-hexene to 2-hexanone are most clearly displayed as graphs of mmol of product (2-hexanone) versus time (in hours). Figure 11 shows the oxidation results characteristic of three [SG]-SH samples which vary in sulfide loading. The samples are referred to by a ratio of sulfide to surface silicon atoms in the silica gel. These values are obtained by assuming complete reaction when functionalizing the gels. However, the experimental sulfide concentration values were always used when determining the mass of silica gel necessary for reaction. Each curve in the oxidation graphs represents many experiments repeated with the same supply of functionalized silica gel. Also, other samples were prepared and compared to previous gels. The experimental sulfide concentrations were very similar between silica gel batches. The idealized S/Si ratios are then used for convenience in referring to several different supplies of similar silica gels.

In Figure 11, if all of the rhodium and copper is effectively site isolated on these samples, then very similar activity should result from each of the catalysts. The 1S/40Si (0.025 mmol S/g[SG]) sample, curve A, is less active

Figure 11. Profiles for the oxidation of 1-hexene obtained at 70°C using [SG]-SH supported rhodium catalysts with various loadings of organosulfide. (A) 1 surface sulfide/40 surface silanol groups, 1S/40Si; (B) 1S/20Si; (C) 1S/10Si.


A IS/40 Si
B IS/20 Si
C IS/10 Si
mmol 2-hexanone
time, hr
0
0.4
0.8
1.2
1.6
2.0
2
4
6
8
10
12
14
16
18
20
22
24
A
B
C

for 2-hexanone production than the 1S/20Si and 1S/10Si samples (0.05 and 0.10 mmol S/g[SG]). This results from diffusion problems which will be discussed further later in this chapter. Curves B and C do show similar activity for 24 hours as shown. Catalytic activity resulting from immobilization of the rhodium and copper complexes on silica gel certainly has been demonstrated, and several comparisons to these results will be made in following sections.

After establishing supported activity, it is important to check for leaching of the metal complexes from the solid into solution. Catalytic oxidations were run for three hours and the solutions removed by syringe under reaction conditions. The filtrate, after measuring the volume, was then placed in a new Parr bottle with another equivalent of Cu(II) and the oxidation re-started in the original manner. The filtrate had activity ranging from 5 to 15 percent of the total normal supported activity depending on the silica gel sample being studied. Since the homogeneous rhodium/copper oxidation catalyst is much more active than the corresponding supported system, then it is apparent that the vast majority of the heterogeneous catalytic activity is due to [SG]-SH bound catalyst.

It is relevant to stress that experiments to check for leaching must be done under reaction conditions. The chemical equilibria involved in leaching may be greatly affected by conditions milder than those during reaction and

thus leaching should be investigated only under reaction conditions.

Alkyl Covering of the Silica Surface to Improve Site Isolation and Catalysis

The silica gel supported catalytic system as described until this point offers several characteristics which make it ideally suited for further investigation of site separation in a quantitative manner. Already demonstrated has been a method for determining the surface loading of organosulfide functional groups, a spectroscopic technique for establishing the identity of silica gel immobilized rhodium species, and an oxidation reaction which can accurately measure catalytic activities and catalyst lifetimes. Thus, any further attempts to alter the silica surface may be monitored rather precisely.

The general supposition that increased site isolation of the silica gel supported rhodium species is directly related to increased catalytic activity is supported by the results obtained using [SG]-SH as the support. Very highly loaded [SG]-SH samples produce catalytic systems of very low activity. Further manipulation of the silica gel supports in order to produce better and/or longer lived site isolation was greatly desired. It was assumed that the general deactivation of the supported catalysts was dependent to some degree upon the aggregation, over time, of rhodium species on the silica surface. A mechanism could be logically postulated whereby sulfide bound rhodium species exchange

with surface silanol protons and thus migrate along the surface until aggregation occurs. As a result, a modification of the silica surface was sought which could remove this possible path of aggregation. One other goal was to obtain a method for increasing the loadings of site isolated species per gram of silica support.

The functionalization of unused surface silanol (-SiOH) groups with alkylsilane moieties results in an effective method for achieving the previously stated goals. Chloroalkylsilanes are utilized to produce alkyl groups bound to the silica surface. The reaction of the alkylchlorosilanes with the silica surface is identical to the surface reaction with (3-mercaptopropyl)trimethoxysilane as described in reactions 1-3. The chloro group here reacts as does the methoxy group in those reactions, forming HCl instead of CH_3OH. Chlorotrimethylsilane, chlorotriethylsilane and chlorotripropylsilane were each used to prepare silica gel samples, along with the same (3-mercaptopropyl)trimethoxysilane in each case. Samples prepared with alkyl groups and the sulfide functionality on the silica surface will be generally referred to as alkylated [SG]-SH, while those with only sulfide will be called either non-alkylated [SG]-SH or merely [SG]-SH. The functionalized silica gels will also be identified by a ratio of surface sulfur to surface silicon (S/Si) as described previously (e.g., 1S/10Si, 1S/20Si). The alkylated gels will also be referred to by a percent alkylation which is the percent of all unused surface silicon

atoms reacted with chloroalkylsilane assuming complete reactions. The assumption of complete reaction is generally supported by elemental analyses for carbon which became possible at levels of substantial alkylation.

Quantitative analyses for sulfide were also done for alkylated [SG]-SH samples. The values of mmol S/g [SG] for these were generally slightly lower than for their non-alkylated analogs. Again, the values obtained for sulfide content were used to determine the necessary quantity of silica gel for catalytic oxidations.

Infrared spectroscopy provided a good deal of information concerning the properties of the alkylated [SG] -SH gels. As described earlier, reaction of $Rh(CO)_2S'_nBF_4$ (S' = solvent) with [SG]-SH samples provides species whose infrared spectra are quite useful. Rhodium species bound to 1S/40Si and 1S/20Si [SG]-SH gels produce the two band infrared spectrum indicative of the monomeric supported complex using both non-alkylated and alkylated [SG]-SH samples. The IR spectrum which results using 1S/10Si non-alkylated [SG]-SH indicates the presence of primarily dimeric rhodium complex on the silica surface. This generally supports the estimation discussed earlier in this chapter that the silica surface must be on the average about 1S/9Si or more dilute in order to produce a system in which most of the rhodium is site isolated. The alkylated [SG]-SH gels (e.g., 80% methylated) produce the monomeric rhodium complex on the surface as indicated by their infrared

spectra. The alkyl surface covering allows the formation of a different surface species than its non-alkylated analog at identical loadings of metal per gram of silica gel. A mixture of monomeric and dimeric rhodium complexes is present on the surface of 80% methylated 1S/5Si [SG]-SH, while primarily the dimer is produced on 80% methylated 1S/2.5Si [SG]-SH. These infrared spectra are shown in Figure 12. It may then be concluded that the alkyl covering cannot prevent rhodium dimerization on the silica surface past a certain level of metal loading on the silica gel.

Catalytic Oxidations Using Alkylated Silica Gels as Solid Supports

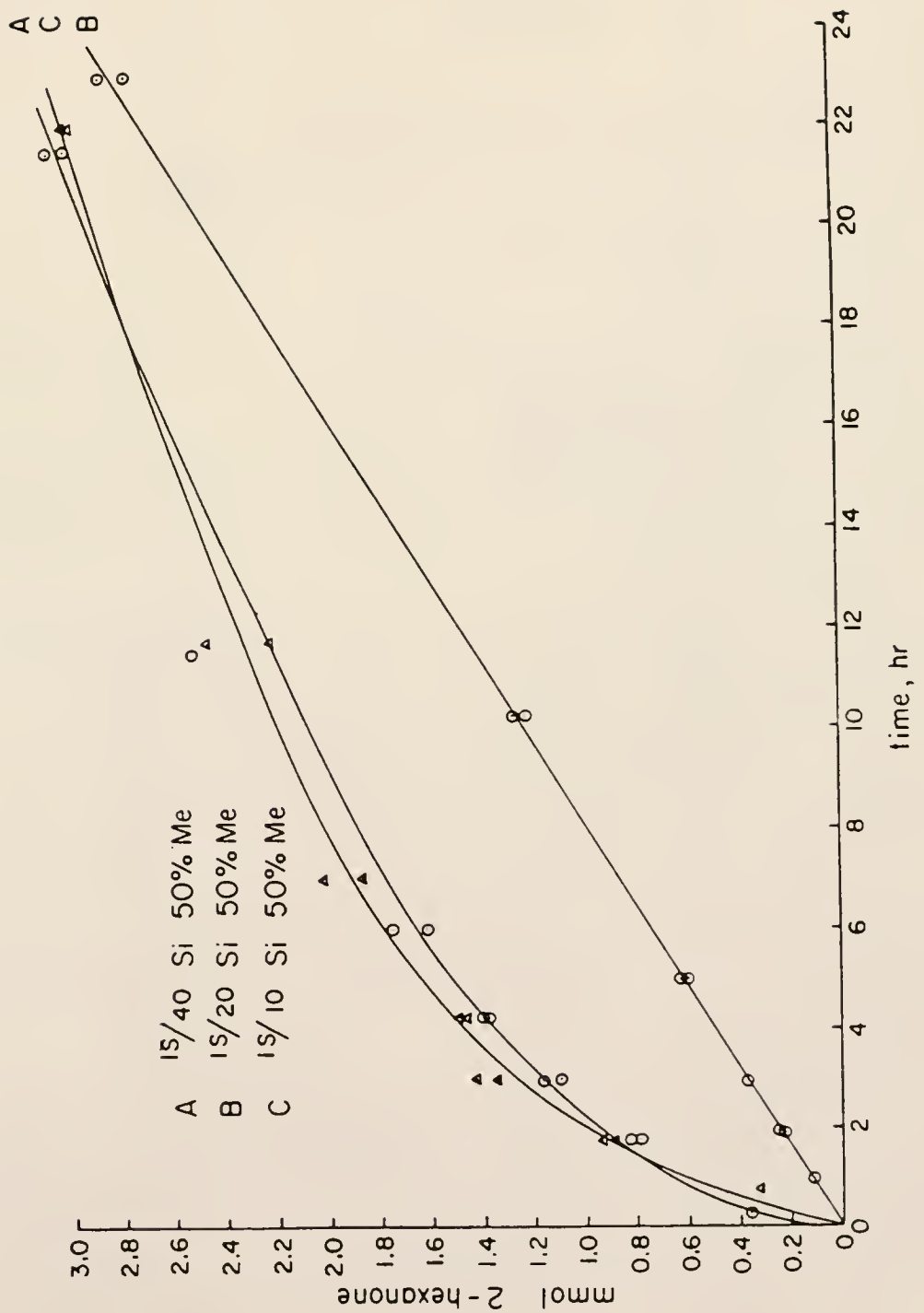
The experimental procedures for conducting catalytic oxidations using alkylated [SG]-SH supports are identical to those for the non-alkylated systems described in Section B.2. Again, the most effective way to present data for these catalytic oxidations is in the form of graphs of millimoles of 2-hexanone product versus time as measured in hours.

The oxidations obtained using [SG]-SH with 50% of its available surface covered with trimethylsilyl group (50% methylated) as supports for the rhodium and copper cocatalysts are shown in Figure 13. Not only do these catalysts demonstrate much greater initial activity in some cases than their unmodified (non-alkylated) counterparts in Figure 11, but they are still more active after 24 hours. The 1S/20Si (0.05 mmole S/G [SG]) 50% methylated gel in curve

Figure 12. Infrared spectra for immobilized $[Rh(CO)_2(C_2H_5OH)_n]BF_4$ using [SG]-SH supports with (A) 1S/10Si 50% Me; (B) 1S/5Si 80% Me; and (C) 1S/2.5Si 80% Me.

A IS/10Si 50% Me
B IS/5Si 80% Me
C IS/2.5Si 80% Me
2300
2000
1800
(cm⁻¹)

Figure 13. Oxidations using [SG]-SH supports which have some portion of the silica surface covered with trialkylsilyl groups. (A) 1S/40Si 50% Me; (B) 1S/20Si 50% Me; (C) 1S/10Si 50% Me.


A
C
B
A 15/40 Si 50% Me
B 15/20 Si 50% Me
C 15/10 Si 50% Me
mmol 2-hexanone
time, hr
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
0
2
4
6
8
10
12
14
16
18
20
22
24

B produces virtually linear 2-hexanone production over 24 hours. Compared to the non-alkylated catalyst curve B of Figure 11 on almost two-fold increase in product has been obtained after 24 hours and a very active catalyst remains. At the end of four hours essentially the same amount of 2-hexanone had been produced by curve B in Figures 11 and 13. Infrared spectra indicated that in both catalysts the essential species was monomeric rhodium complex before the start of catalysis. Thus, alkylation of silica gel in this instance has greatly enhanced catalyst lifetime.

Comparison of 1S/10Si catalyst systems from curve C of Figures 11 and 13 reveals that the methylated catalyst is superior almost from the very start of the oxidation. This result correlates well with the fact that the non-alkylated catalyst is composed of rhodium dimer, while the alkylated one contains monomeric rhodium before reaction. This demonstrates that higher loadings of catalytically active complex can be obtained under site isolated conditions by diluting the functionalized reagent in the hydrocarbon matrix formed by $-Si(CH_3)_3$. A very active catalyst is still present after 24 hours.

A surprising result is represented by curve A in Figures 11 and 13. According to infrared spectroscopy site isolation (rhodium monomer) exists in both systems before reaction. The diffusion problem described in relation to Figure 12 has apparently been decreased by the greater affinity of alkene for the alkylated surface than for

solvent. Such a rationalization explains the greater initial activity of curve A in Figure 13 versus Figure 11 as well as the increased activity after 24 hours.

Figure 14 shows the results of 1-hexene using catalysts supported on 50% and 80% ethylated silica gels. They are generally more active than the non-alkylated gel catalysts and are still very active after 24 hours. The 1S/10Si 80% ethylated catalyst (curve E) is less active and the 1S/20Si 80% ethylated gel (curve D) more active than might have been predicted. Samples which were 80% methylated yielded results similar to those of the 50% methylated gels. It is also seen in Figure 14 that increasing the percent alkylation does not have a drastic effect on catalytic activity.

The 80% propylated [SG]-SH samples produce catalytic results very much like those of the non-alkylated silica gels of Figure 11. Figure 15 displays oxidations run for longer time periods, each done with 1S/20Si [SG]-SH gels which have different surface modifications. The 80% methylated gel (curve B) is still active after 140 hours. It can be seen that the 80% ethylated gel is less active than the methylated one, while the propylated catalyst is nearly identical to the non-alkylated sample. The propylated silica gels, and to a lesser extent the ethylated ones, are markedly slow in "wetting" by ethanol. Perhaps it is this increased hydrocarbon-like nature of the surface which accounts for their decreased efficiency as catalytic supports relative to the methylated gels. Thus, even though enhanced solubility

Figure 14. Oxidations of 1-hexene using [SG]-SH samples as supports. (A) 1S/40Si 50% Et; (B) 1S/20Si 50% Et; (C) 1S/10Si 50% Et; (D) 1S/20Si 80% Et; (E) 1S/10Si 80% Et.

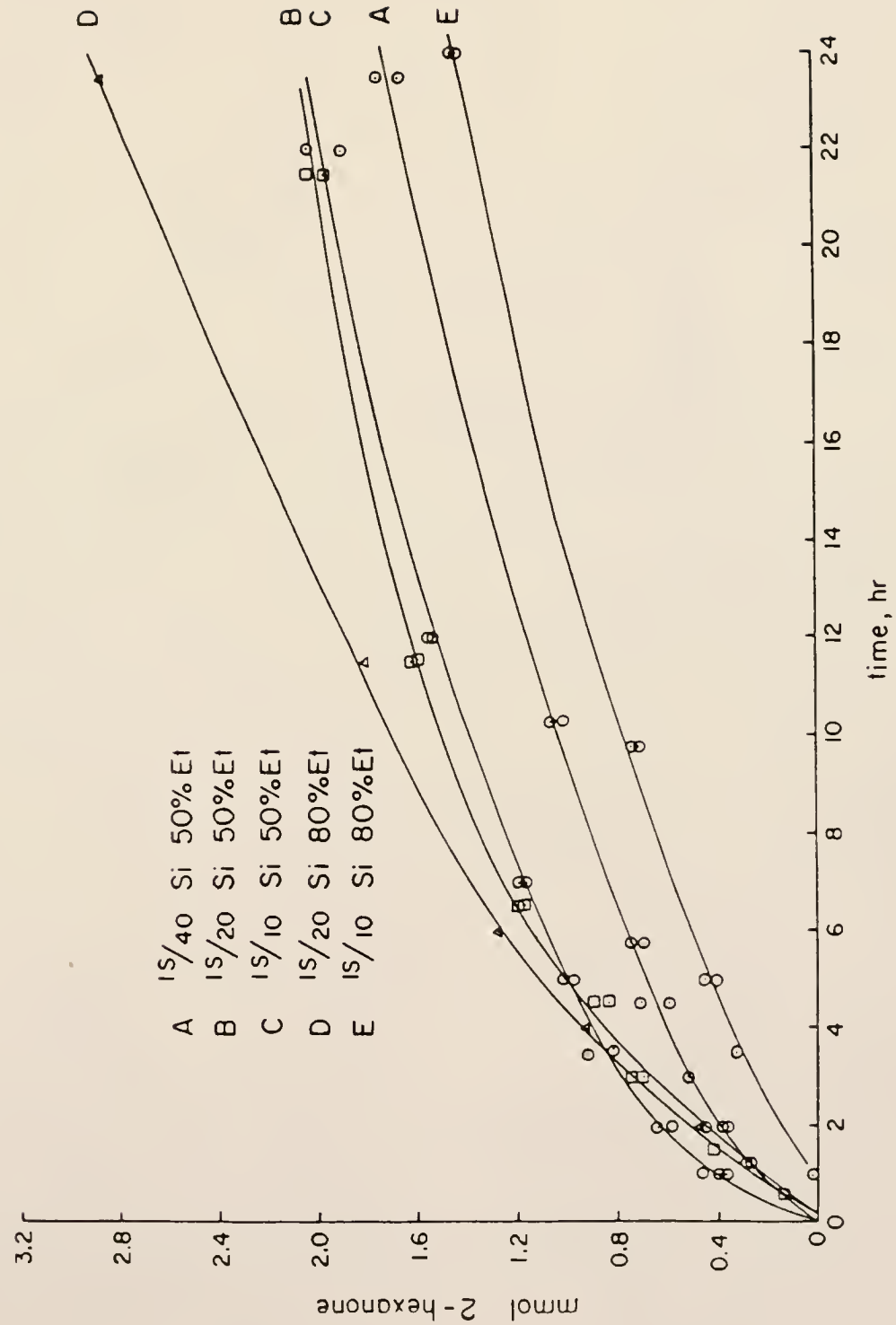
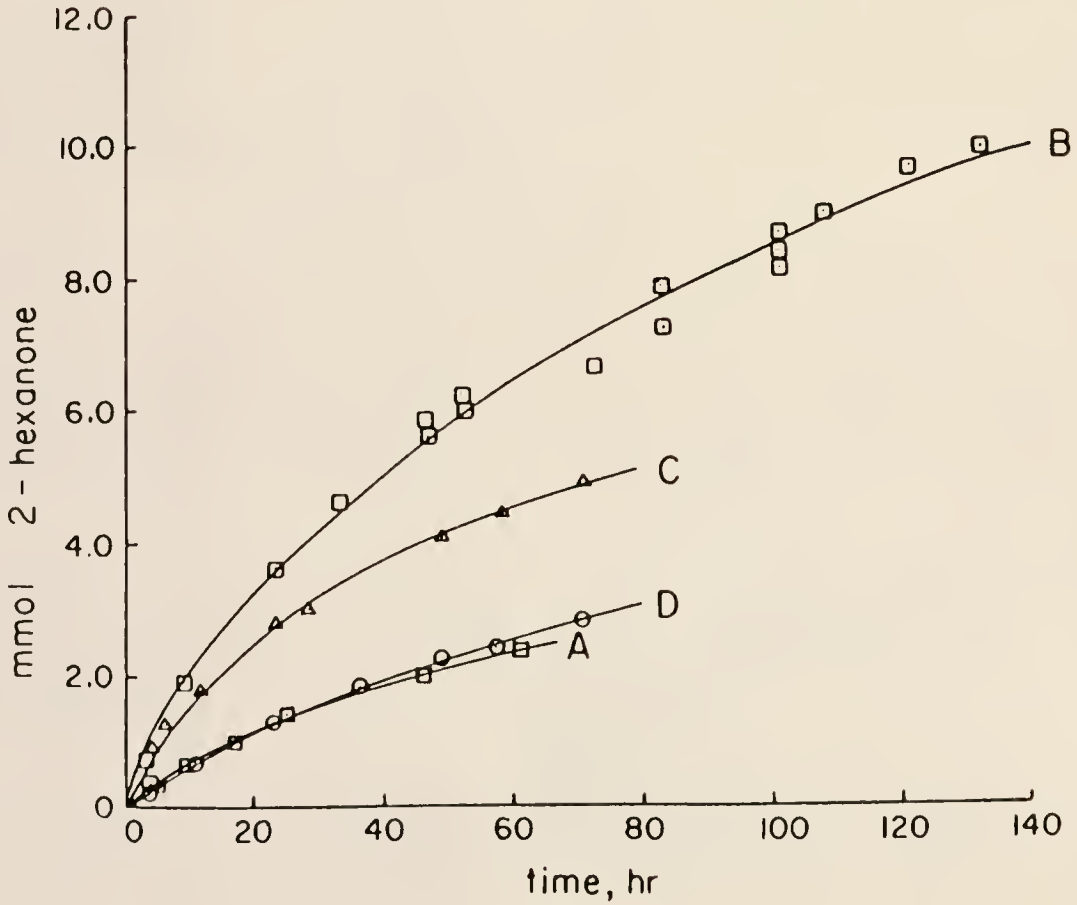

A IS/40 Si 50% Et
B IS/20 Si 50% Et
C IS/10 Si 50% Et
D IS/20 Si 80% Et
E IS/10 Si 80% Et
mol 2-hexanone
time, hr
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
2
4
6
8
10
12
14
16
18
20
22
24
A
B
C
D
E

Figure 15. Oxidations of 1-hexene over longer time periods. (A) 1S/20Si not alkylated; (B) 1S/20Si 80% Me; (C) 1S/20Si 80% Et; (D) 1S/20Si 80% Pr.

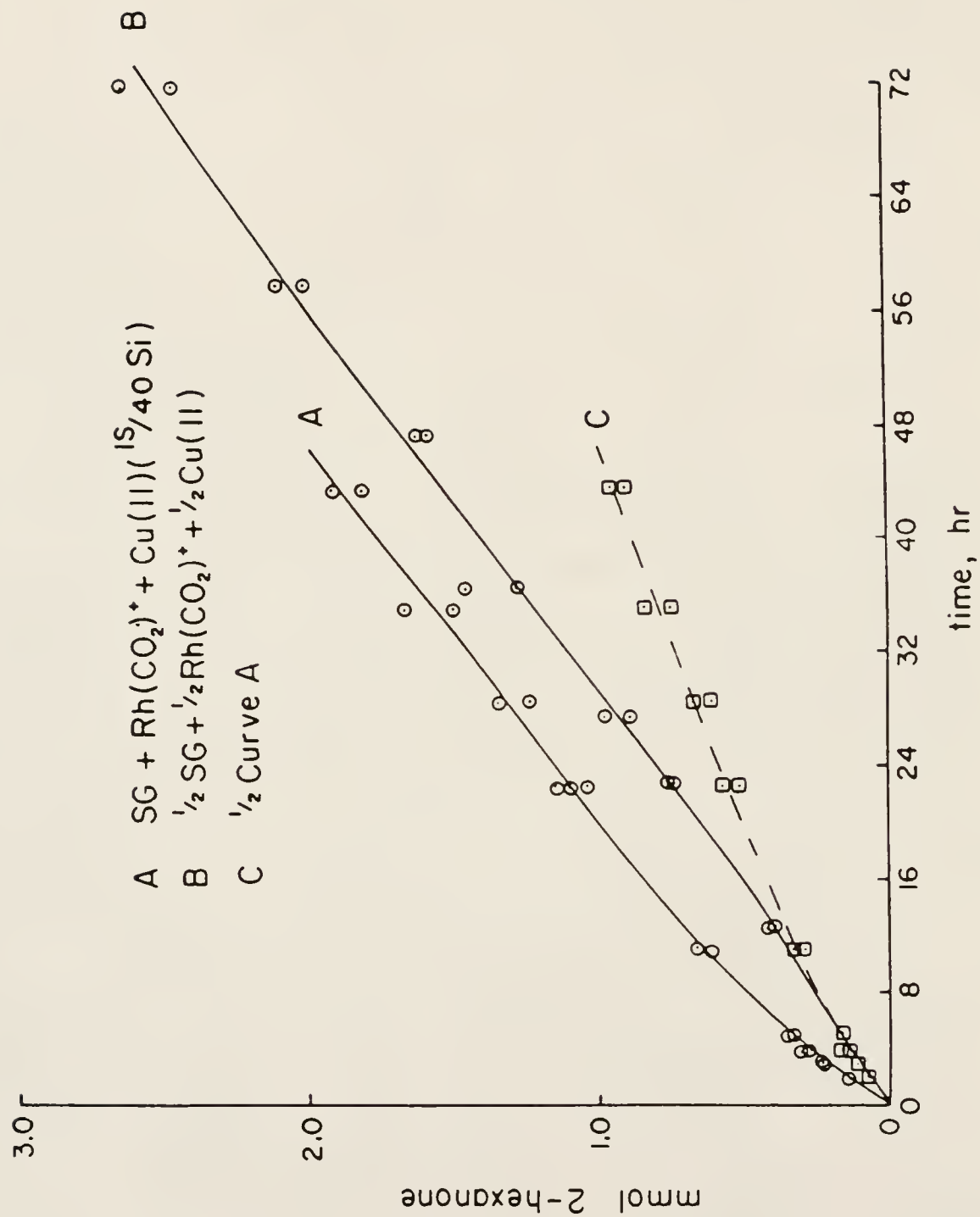
A IS /20 Si Not Alkylated
B IS /20 Si 80 % Me
C IS /20 Si 80 % Et
D IS /20 Si 80 % Pr



of the alkene in the surface layer may occur, exclusion of the solvent would inhibit the reaction.

An investigation was undertaken to determine whether under conditions in which the large amounts of silica gel used in 1-hexene oxidations when the 1S/40Si (0.025 mmol S/g [SG]) gels are employed as catalyst supports diffusion might become rate-controlling. A typical 1-hexene oxidation employing 1S/40Si non-alkylated [SG]-SH was run. A second oxidation using one-half the amount of rhodium and copper, and thus one-half of the silica gel support, was also run. All other initial conditions and amounts of reactants were identical. Assuming that diffusion is not rate-controlling the rate of this oxidation should have been one-half of the original rate since the oxidation is first order in rhodium concentration.[63] Figure 16 clearly shows the reaction with one-half of the silica gel supported catalyst to have a rate greater than one-half of the normal oxidation. The dashed line C is one-half of the curve A. Thus, there seems to be some reaction inhibition due to the large amounts of silica gel support used in the 1S/40Si oxidations (9-12 g), which is near the limit of the mass of gel which may be stirred in this experimental apparatus. This result may be ued to help explain why in general several 1S/40Si (0.025 mmol S/g[SG]) supported catalysts are not as active as their 1S/20Si (0.05 mmol S/g[SG]) counterparts (e.g., Figure 11).

Figure 16. Oxidations of 1-hexene used to investigate diffusion problems. (A) A "typical" 1-hexene oxidation using 1S/40Si [SG]-SH; (B) oxidation using one-half of the amounts of 1S/40Si [SG]-SH, rhodium catalyst and copper(II) used in (A); (C) a representation of one-half of curve A.


A SG + Rh(CO2)2* + Cu(II)(IS/40 Si)
B ½ SG + ½ Rh(CO2)2* + ½ Cu(II)
C ½ Curve A
A
B
C
mmol 2-hexanone
time, hr
0
1.0
2.0
3.0
8
16
24
32
40
48
56
64
72

Possible Effects of a Different Rhodium Catalyst Characterization

The design and implementation of the supported catalytic systems have been based on Mimoun's characterization of the active catalyst as a rhodium(I) complex. The possible characterization of the catalyst as a rhodium(III) species as discussed in Chapter II may have several implications. Chloride ion may also be quite important since 3-5 equivalents of chloride ion promote better homogeneous oxidations using $[Rh(CO)_2S'_n]BF_4$ (S' = solvent) and given that the most stable homogeneous catalyst species may be rhodium chloride complexes of same type.[64] Chloride ion cannot be added to the [SG]-SH systems without extensive leaching occurring. The possible use of a supported multi- dentate ligand for the immobilization of a rhodium(III) catalyst should be considered for future use. It would also be of interest to compare the effects of alkylation of a multidentate ligand silica gel support to those presented here for a monodentate ligand system.

Conclusions

The spectral properties and catalytic behavior of the described systems demonstrate that isolating functionalized [SG]-SH groups with $[SG]-SiR_3$ (where R is alkyl) leads to some very pronounced changes. The stability of the methylated catalysts is greatly enhanced over that of the

non-alkylated systems. On non-alkylated [SG]-SH it is possible that the derivatized silanol groups may exchange with protons on nearby silanol groups and thus migrate along the surface, aggregate and become inactive. The alkylated gels remove -OH groups and would be able to effectively suppress such a process leading to a longer lifetime for site-isolated conditions. The mixing of reagents prior to functionalization also ensures a better distribution of functional groups over the surface under site isolated conditions and enables one to attain a more concentrated site-isolated catalyst.

In the specific catalytic system studied, increasing the length of the alkyl chain covering the silica surface to ethyl and propyl decreases catalytic activity over the methyl covering. This may be due to solubility properties as discussed earlier, or perhaps due to increased efficiency at keeping the two cocatalysts apart. This approach should still find general application and utility in the area of hybrid catalysts where site isolation is a desired feature.

Experimental

General Procedures

All solvents and reagents were of reagent grade and used without further purification unless otherwise specified. The $[Rh(CO)_2Cl]_2$[41] and $[Rh(CO)_2S'_n]BF_4$[62] (S' = solvent) were prepared as reported in the literature or purchased from Aldrich and recrystallized from n-hexane. The $(CH_3O)_3Si(CH_2CH_2CH_2SH)$ and $ClSi(CH_3)_3$ were obtained from Aldrich and $ClSi(C_2H_5)_3$ and $ClSi(C_3H_7)_3$ from Petrarch Systems. Silica gel was grade 62 from Davison Chemical.

Infrared spectra were recorded on a Perkin-Elmer model 283B infrared spectrometer. The GLC were obtained with a Varian model 940 FID instrument using a 3m, 1/16 in. i.d. copper column packed with Chromasorb P supported diethylene glycoladipate or with a Varian model 3700 FID chromatograph using an 8 ft, 1/8 in. column of the same material. The 2-hexanone production was quantified using 2-heptanone as an internal standard. Electronic absorption spectra were taken on a Cary 14, and all samples were run in air at ambient temperatures and pressures.

Preparation of Silica Gel Supports

All reactions of functionalizing silanes with silica gel were done under argon with xylenes as solvent. Silica gel was stirred in xylenes under argon, followed by heating, and then a solution of one or more silanes in xylenes was

added dropwise to the hot silica gel slurry. The non-alkylated [SG]-SH gel was made by adding $(CH_3O)_3Si(CH_2CH_2-CH_2SH)$ to the gel. The [SG]-SH alkylated gels were made by adding a solution of the mercaptosilane mixed with R_3SiCl (R= CH_3, C_2H_5 or C_3H_7). This technique is preferable to adding each silane in separate steps. After refluxing 24 hours, the silica gels were thoroughly washed with xylenes, ethanol and then dried at $\sim 90^{o}C$. The silica gels remain white in appearance.

Determination of -SH on Silica Gel

Silica gel and its surface silanol groups were reacted with $(CH_3O)_3Si(CH_2CH_2CH_2SH)$ to produce the $[SG]-OSi(OCH_3)_2-(CH_2CH_2CH_2-SH)$(abbreviated as [SG]-SH). R_3SiCl (R=methyl, ethyl or propyl) was used to complete reaction of the silanol groups and cover the silica gel surface with alkyl groups. Evidence that trialkylsilyl groups are bound to the surface is obtained by a substantial increase in the percent carbon found in the elemental analyses and by an increase in the lifetime of the functionalized catalyst.

Electronic absorption was used to determine the amount of sulfide on each silica gel sample ([SG]-SH). The [SG]-SH samples were stirred with freshly prepared $[Rh(CO)_2S'_n]BF_4$ (S' = solvent), the solid filtered off and the electronic absorption spectrum of the filtrate taken. From a calibration curve of the rhodium complex concentration versus its absorbance at 390 nm the amount of rhodium in the filtrate is measured. The amount of rhodium on the gel is

determined by the difference of the known initial amount of rhodium and the amount of rhodium in the filtrate. Assuming complete reaction of one rhodium per sulfide, the amount of rhodium is equal to the amount of sulfide on the silica surface. An analysis of this type was done for all samples.

Samples were prepared which varied in surface sulfide concentration and in percent of available surface silanol groups which were "alkylated" (reacted with trialkylchlorosilane). Assuming tetrahedral coordination around silicon and oxygen atoms with an approximate silicon-oxygen bond distance of two Angstroms, and assuming that as an upper limit a flat surface exists with all surface groups being silanols, a separation of 6.5 Å exists between the oxygens of surface hydroxyl groups. This corresponds to one surface hydroxyl per 4.3×10^{-19} m^2 of surface so it can be calculated that as an upper limit there are about one mmol surface silanol group atoms per gram [SG]. With this value it can be determined that the [SG]-SH samples prepared contain approximately 1/40, 1/20, 1/10 and 1/5 millimoles sulfide/millimole surface Si (S/Si) which corresponds to 0.025, 0.05, 0.10, 0.20 and 0.40 mmol S/g[SG]. Silica gel samples used as catalytic supports will be referred to by a (S/Si) ratio and by a number of mmole S/g[SG]. In some instances the percent alkylation (methylation, ethylation or propylation) of the surface silicon sites will also be used.

Catalytic Oxidations of 1-Hexene

All catalytic 1-hexene oxidations were run in 250 mL Parr pressure bottles equipped with brass Swagelok pressure heads. These were constructed to allow purging with O_2, as well as sampling of the solution under reaction conditions during the course of the reactions. The 2-hexanone production was measured by GLC.

All catalytic reactions were run using 0.074 mmol $[Rh(CO)_2S'_n]BF_4$ (prepared as reported earlier and used immediately) and 0.0179 g $Cu(NO_3)_2 \cdot 3H_2O$ (0.074 mmol). The amount of silica gel employed was varied to provide enough -SH sites to bind all of the rhodium and copper with a 10% excess (e.g., 4.9 g of 1S/20Si 80% Et [SG]-SH). Both metal ions are attached to the [SG]-SH samples through the -SH moiety producing a lemon-yellow to yellow-green supported catalyst. The catalyst was added to a 250 mL Parr bottle along with 0.32 mL 0.47 M $HClO_4$ (0.150 mmol, as an ethanol solution prepared from aqueous conc. $HClO_4$), 1.136 mmol 2-heptanone, 45 mL absolute ethanol, and 15 mL 1-hexene (purged through alumina to remove peroxides). This mixture was purged 5 times with 60 psi O_2, set to 40 psi O_2, and the reaction initiated by placing the system in a 70°C oil bath.

CHAPTER IV
THE SYNTHESIS AND CATALYTIC APPLICATIONS OF A MULTIDENTATE LIGAND AND CORRESPONDING METAL COMPLEXES BOUND TO SILICA GEL

Introduction

The use of a polymer as a support for catalysts was discussed in Chapter III for a specific system which employed a monodentate chelate on silica gel. The general use of polymers as supports for catalysts and chelates, and also as synthetic reagents, has developed enormously since their use in peptide synthesis was shown by Merrifield approximately twenty years ago.[65] It was generally assumed for several years that there was little, if any, interaction between functionalized sites on resins such as polystyrene. This is now known not to be the case, and Chapter III demonstrated some of the rather stringent conditions which must be met in order to achieve site isolation on a support such as silica gel.

Another general approach to preparing stable polymer bound metal complexes is that of first attaching a multidentate ligand system to a polymer backbone and then adding the metal ion to the previously formed ligand. There have been many reports discussing polymers which contain chelating groups of various sizes and donor atoms.[66-69] An excellent review of this area is cited here as reference 70. Most of the polymer bound chelates studied are mono- or bidentate, with only a few tri- and tetradentate systems having been investigated.[69b,71] Resins with bidentate chelate groups often must provide a metal ion with two or three chelating groups since many metal ions prefer forming four or six coordinate complexes. This led to the common use of uncrosslinked or lightly crosslinked polymers. The ambiguity involved in trying to characterize these polymer bound metal complexes makes it very difficult to interpret data from catalytic reactions or physical methods.

In virtually all of the literature reports cited in this area, there is no attempt made to isolate functionalized sites from one another and in many cases two or more sites must interact in order to provide successful chelation.

Chapter III discussed in detail the conditions required to achieve site isolation on silica gel and surface modifications which may enhance that isolation. The initial sections of this chapter will discuss the preparation of a stable multidentate ligand site isolated on silica gel which can complex a variety of metal ions into polymer bound

complexes of a known geometry. Investigations of several applications of these polymer bound complexes will then be presented, followed by investigations into the use of different solid matrices as chelate metal complex supports.

The ligand prepared on silica gel is a pentadentate ligand which complexes several different metal ions. The silica gel supported complex of iron(III) was used to investigate some known homogeneous reactions.

Biological oxidation processes are generally quite selective and sensitive and as a result attract the attention of many chemists.[72] Cytochrome P-450 is one enzymatic system which can catalyze several types of oxidative transformations, including selective alkane hydroxylations and has therefore been an object of much research effort. Several studies have proposed intermediate high-valent oxometalloporphyrin species in the catalytic cycles of several heme-containing oxygenase enzymes.[73,74] Simple chemical models for cytochrome P-450 were sought in order to provide insight into some of the basic processes involved in its chemical reactivity. A significant finding was the realization that iron,[75] chromium,[76] and manganese[77] porphyrins could catalyze oxygen transfer from iodosylbenzene to simple hydrocarbons.[78] In all of these cases, a metal-oxo species is proposed as an intermediate, although complete mechanistic details have not been determined. However, it was the possibility of generating silica gel supported iron or manganese oxo species to achieve some type of oxidative

transformation which was the impetus behind the work reported here. The ability to form supported cobalt-dioxygen complexes (vida infra) helped to encourage the idea that it would be sterically possible to generate the supported iron or manganese oxo intermediates. Another goal was to determine the effect of limiting or eliminating interaction between metal centers via their support and site isolation on silica gel.

Another topic briefly investigated is the long known "Fenton chemistry" of iron salts and hydrogen peroxide affecting the hydroxylation of organic substrates.[79] This area has recently been reinvestigated by Cheves Walling and he gives an excellent overview of this area in reference 80. The original goal of achieving this type of peroxide induced oxidation with a supported iron complex was not realized due to the leaching of metal complex into solution in the presence of acid and peroxide. Thus, no mechanistic or catalytic information is provided, although some further knowledge of the silica surface is obtained.

Catalytic processes which require two different metals have not achieved much success in being supported on polymers. A method which may successfully attain support of both metals is that of incorporating one active metal into the structure of the support while supporting the other metal on the surface of the solid. Incorporation of copper(II) ions into silica gel is described along with attempts at catalysis by resulting bimetallic systems.

The method of electron spectroscopy for chemical analyses (ESCA) holds promise for studying the surfaces of solid catalysts.[81,82] The technique basically involves the measuring of the energy spectrum of the electrons ejected from a sample after bombardment with monoenergetic x-rays. The orbitals of origin of the ejected electrons determine their energies, with each element having characteristic orbital ionization potentials. Thus, comparison of a sample's ejected electron energy spectrum to known spectra usually provides surface analysis and/or molecular structure information. Since x-rays can eject electrons from at most the top 100 Angstroms of a solid, ESCA is well suited for surface studies. The applications of this method to a few of the systems studied here will be discussed in the following sections, and data given which may justify its even wider use in future work.

Results and Discussion

Synthesis of a Salen Ligand on Silica Gel

The synthesis of a multidentate ligand system on a rigid support such as silica gel was derived as a method for possibly achieving properties different than its homogeneous analogs. The ligand described here is a three nitrogen, two oxygen donor which had to be synthesized stepwise on the silica surface. The plain silica surface was first reacted with $(H_3CO)_3SiCH_2CH_2\text{-}(C_6H_4)\text{-}CH_2Cl$ in order to produce the chloromethyl functionality on the surface. In fact the

chloromethyl moiety attached to phenyl groups is similar to the surface of polystyrene. Earlier work in this research group led to the successful support of the desired ligand on polystyrene.[83] However, this polymer was not rigid enough to produce all of the desired characteristics (vida infra). The next step in the ligand synthesis is to react the chloromethyl groups with $HN(CH_2CH_2CN)_2$ (3,3'-iminodipropionitrile) which will be referred to by its common name dicyanoethylamine, DCEA. This reaction does not proceed under routine conditions of mixing the DCEA with silica gel in a solvent under nitrogen. Attempts to react DCEA with chloromethylated silica gel under a normal inert atmosphere leads to the polymerization of the DCEA into a viscous mass accompanied by little DCEA incorporation. Experiments were performed under high argon pressures after concluding that rigorous exclusion of oxygen might be necessary. It was also discovered that Alum and coworkers[50] had reacted the chloropropyl group bound to silica gel with diethylamine at elevated argon pressures to produce the bound tertiary amine. Reaction of the silica gel with pure DCEA (without solvent) in a pressure bottle of the type used for catalysis under 100 psi of argon pressure produced the DCEA bound to silica gel as shown below.

$$[SG]\text{-}CH_2Cl + HN(CH_2CH_2CN)_2 \rightarrow [SG]\text{-}CH_2\text{-}N(CH_2CH_2CN)_2 + HCl \qquad (18)$$

Next, the cyano groups are reduced to amine functionalities by reaction with B_2H_6/THF solutions under nitrogen. This supported ligand is referred to as [SG]-DPT from the common name dipropyltriamine (DPT). The general scheme for the preparation of [SG]-DPT is shown in Figure 17.

Finally, the Schiff base condensation of [SG]-DPT with salicylaldehyde is conducted in order to produce the desired [SG]-SalDPT as shown in Figure 18. This supported ligand is stable in air and the entire silica gel support is pale yellow in color. Thorough washing, Soxhlet extraction and complete drying of the silica gel after each step in this procedure is very important. The [SG]-SalDPT was also prepared with alkylation of the non-reacted surface silanol groups, as were samples which varied in surface concentrations of the -SalDPT ligand. A slight variation of the ligand was synthesized using 3,5-dibromosalicylaldehyde to produce [SG]-BrSalDPT.

Characterization of these supported ligands is not easily attained. The low loadings on the surface often rule out the use of elemental analyses. The best method available routinely is that of incorporating certain metals into the silica bound ligand and comparing their electron spin resonance (ESR) spectra to the spectra of their homogeneous and polystyrene bound analogs. The [SG]-DPT ligand when stirred with copper(II) acetate in DMF binds the metal ion to form [SG]-Cu(II)DPT which is green in color. Similarly, [SG]-Co(II)SalDPT is easily formed by mixing of the silica

Figure 17. General scheme for the preparation of [SG]-DPT.

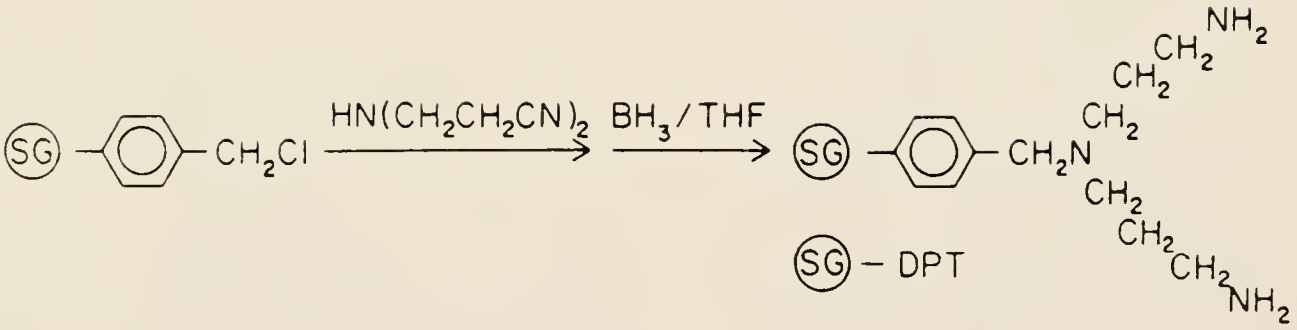
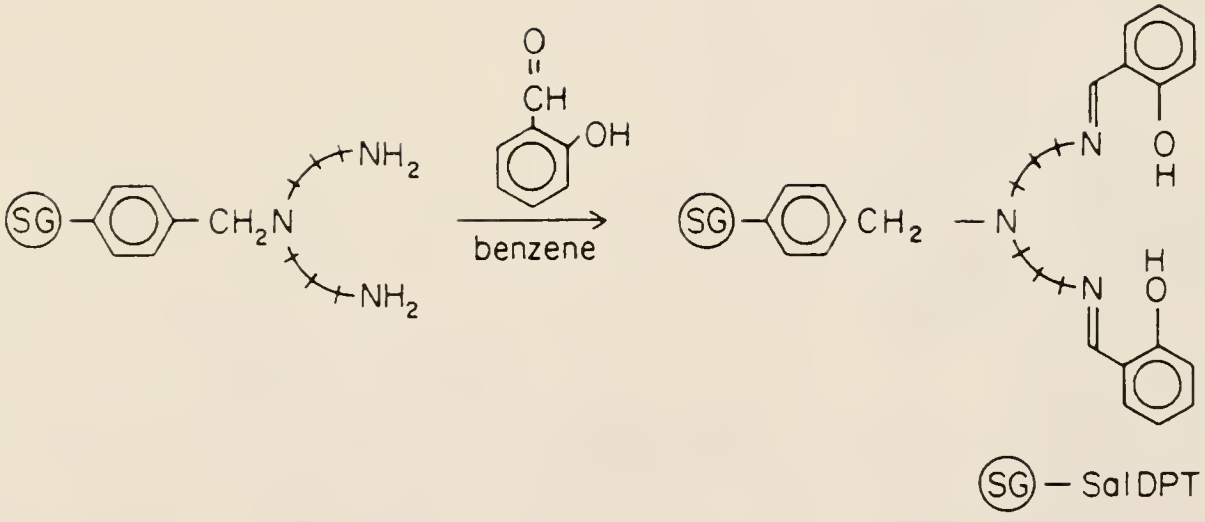

SG
CH2Cl
HN(CH2CH2CN)2
BH3/THF
SG
CH2N
CH2
CH2
CH2
NH2
CH2
CH2
NH2
SG – DPT

Figure 18. The preparation of [SG]-SalDPT from [SG]-DPT.


SG
CH2N
NH2
NH2
O
CH
OH
benzene
SG
CH2
N
N
OH
N
OH
SG — SalDPT

gel supported SalDPT ligand with cobalt(II) acetate in DMF solution. The ESR spectra of these complexes can then be used for characterization to verify that the silica gel supported species have been prepared. The oxygen adduct, [SG]-Co(II)SalDPT·O_2, must be used in order to obtain a spectrum for the cobalt system. The ESR spectra of these silica gel bound complexed are then almost identical to the spectra of the polystyrene bound complexes.[83] The attainment of a stable multidentate ligand which is covalently bound to a rigid silica gel support with site separation achieved by surface alkylation is a development which has many possible applications, several of which will be discussed in the following sections.

Oxygen Transfer Using [SG]-Fe(III)SalDPT and [SG]-Mn(II)SalDPT

Among the general interest in cytochrome P450 oxidations has been specific interest in aromatic and aliphatic hydroxylations, alkene epoxidation, and interest in the nature of the active oxidant. As mentioned previously, most of the systems used to investigate these processes involve iron or manganese tetraphenylporphyrin complexes.[72-78] Since silica gel supported iron(III) and manganese(II) complexes can be easily prepared from the [SG]-SalDPT ligand, these complexes were employed to determine

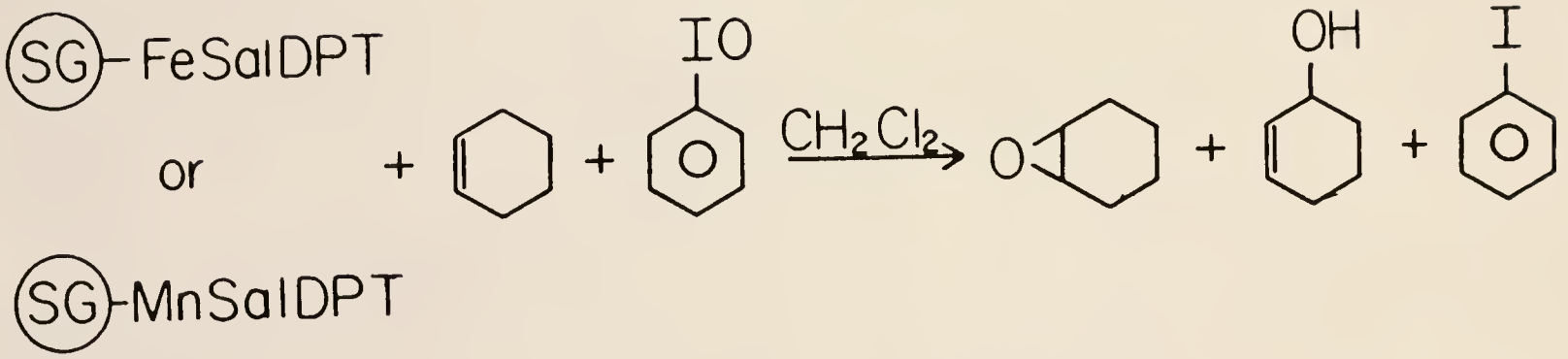
whether they could provide a polymer bound model for any of the above reactivity.

Pressurizing the silica gel supported iron or manganese complexes with dioxygen at 60 psi O_2 and 40°C in methanol produced no oxidation of a cyclohexene substrate. This was not surprising, however, since other oxygen sources are usually required when examining the cytochrome P450 systems. Iodosylbenzene, commonly used, is the oxygen source for all of the results which follow.

Cyclohexene was employed as a substrate in order to investigate epoxidation and hydroxylation of alkenes. Cyclohexene, iodosylbenzene, and a cyclopentanone internal standard were used in methylene chloride solvent along with a polymer supported metal complex. Product formation was determined by use of gas-liquid chromatography, using a carbowax column at 130°C. The retention times varied with fluctuations in gas flow, but the approximate average retention times (in minutes) were the following: 0.8 for CH_2Cl_2, 2.6 for cyclohexene oxide, and 8.7 for cyclohexenol.

The iron(III) complex, [SG]-Fe(III)SalDPT, converted cyclohexene to cyclohex-2-enol and cyclohexene oxide, along with producing iodobenzene from the iodosylbenzene in CH_2Cl_2 at room temperature. The general reaction using [SG]-FeSalDPT or [SG]-MnSalDPT is represented in Figure 19. This supported iron complex achieved oxygen transfer, but also produced an interesting product distribution. Using a homogeneous solution of tetraphenylporphinatoiron(III)

Figure 19. General conversion of cyclohexene to corresponding products in the presence of iodosylbenzene and a supported metal complex.


SG-FeSalDPT
or
SG-MnSalDPT
IO
CH_2Cl_2
O
OH
I

chloride (FeIIITPPCl) Groves et al. reported[75] production of cyclohexene oxide and cyclohexenol in a ratio of 3.7:1 in CH_2Cl_2 at room temperature. The silica gel supported iron(III) produces cyclohexenol almost exclusively, with only trace amounts of cyclohexene oxide formed. The homogeneous system produces 4.2 total turnovers (based on mmol products and mmol metal complex) in the relatively short time period of 1-2 hours.[75] The supported system reacts more slowly, requiring 47 hours to produce 2.4 turnovers of the cyclohexenol product. Also, commonly cited[75] is the destruction of catalyst by iodosylbenzene. This process does not appear to occur to the silica gel bound complexes, in that there is no color loss from the support into solution and the [SG]-FeIIISalDPT resin when re-used several times produces identical results each time in terms of the amount of product formed and the rate of product formation.

The silica supported manganese complex, [SG]-MnSalDPT, also converts cyclohexene to cyclohexenol and cyclohexene oxide. In this system, however, only cyclohexene oxide is produced for the first 30-45 hours after iodosylbenzene addition. Cyclohexenol is then produced relatively quickly until the cyclohexenol to cyclohexene oxide ratio is 1.3:1 after approximately 53 hours of reaction. The supported system yields 1.4 turnovers of exclusively cyclohexene oxide by the end of 45 hours, but after 53 hours has produced 2.1 turnovers of the cyclohexene oxide product and 2.7 turnovers of the cyclohexenol product. The supported Mn(II) system's

reactions were conducted under a nitrogen atmosphere. The re-use of [SG]-MnSalDPT samples indicated the activity of the used silica gel and showed no evidence of color loss into solution. The yield of products was only monitored approximately every 12 hours during re-use, but indicated the same 1.3:1 product ratio of cyclohexenol to cyclohexene oxide produced at approximately the same rate as the original reaction had during its last hours. Cyclohexane is not oxidized by either the supported iron or manganese systems under the conditions used for cyclohexene oxidation.

A product of the reaction of ClMn(III)TPP derivatives with iodosylbenzene is $[ClMn(IV)TPP(OIPh)]_2O$, which is capable of oxidizing alkane and alkene substrates at room temperature under an inert atmosphere.[84] Reaction of the manganese dimer above with cyclohexene produces the following oxidation products in one hour: 3-chlorocyclohexene, 32%; cyclohexenol, 7%; cyclohexene oxide, 31%; 2-cyclohexen-1-one, 1% (percents based on three oxidizing equivalents for the dimer). The incorporation of chloride into a product, along with the relatively small production of cyclohexenol, are results which differ from those of the silica gel supported system. Both the homogeneous iron and manganese TPP complexes yield products which contain anions which have been incorporated from the TPP complexes. Obviously, the lack of anions from the supported metal complexes excludes the possibility of formation of any analogous products by the supported systems.

In conclusion, the product distributions and lack of catalyst degradation make the silica gel supported SalDPT iron and manganese complexes, despite their slower rate of activity, both interesting and worthy of further investigations. Future adjustment of metal complex concentrations or reaction conditions might provide progress toward activation of alkanes by these heterogeneous catalysts.

Synthesis of [SG] -Fe(II)SalDPT

Complexes of iron(II) are of great interest, although they are generally difficult to prepare as air stable compounds. Previous attempts to prepare crystalline Fe(II)-SalDPT resulted in irreversible oxidation presumably to the oxo-bridged dimer. Preparation of Fe(II)SalDPT immobilized on a rigid silica gel support was desired in order to compare its properties to those of the attempted crystalline analogs.

Great care must be used to eliminate oxygen when preparing the supported iron(II) complex. Performing cycles of a freeze-pump-thawing procedure on [SG]-SalDPT in DMF solvent is the best way to exclude oxygen initially. The compound $Fe(CO)_5$ is employed as the source of iron and is reacted with the silica gel supported ligand in Schlenk-type apparatus. After reaction, filtering and thorough washing (see Experimental Section) a purple/pink silica gel results. This silica gel is very different in appearance from the [SG] -Fe(III)SalDPT complex which is a tan/brown color. Samples

of [SG]-SalDPT with 80% of its surface methylated (covered with $-Si(CH_3)_3$ groups) and 0.05 mmol ligand per gram [SG] (1 ligand/20 surface Si) were used to prepare the iron(II) complex in order to provide a surface which should have site isolation of the iron centers (see Chapter III for details of the alkylation process). The SalDPT ligand is attached to a longer chain of atoms, and occupies a larger area, than the sulfide ligand ([SG]-SH) discussed in Chapter III. As a result, it is theoretically able to cover a greater area (780 A^2) than the sulfide ligand and therefore requires a loading of 1 ligand/18 surface SiOH or more dilute in order to achieve site isolation. This is the loading necessary to avoid any contact between ligands; however, alkylation of the silica surface very likely allows site isolation at higher ligand loadings. The larger steric bulk of the multidentate ligand may also allow some amount of ligand-ligand contact without the corresponding metal center interaction.

Mossbauer spectroscopy was used to help determine the oxidation states of iron in silica gel supported species.[85] Spectra of supported complexes prepared with Fe(III) give data indicative of an Fe(III) complex. The spectra are not very intense or sharp due to the relatively low loading of iron used to obtain site isolation coupled with the fact that only the 2% abundant ^{57}Fe isotope of iron is Mossbauer active. The silica gel supported Fe(III) complex yields Mossbauer spectra very close to those reported for similar polystyrene bound Fe(III) complexes.[83]

The Mossbauer spectrum of a small [SG]-Fe(II)SalDPT sample sealed under nitrogen was not intense enough to provide a meaningful characterization.

The goal of preparing the [SG]-Fe(II)SalDPT complex was to obtain site isolation of the iron centers and thus remove the possibility of forming any type of oxo-bridged dimer when exposed to oxygen. However, the supported iron(II) silica gel turns from its original pink color to the tan color of supported iron(III) within minutes upon exposure to air. This change is non-reversible by treatment with vacuum and the change also occurs at liquid nitrogen temperatures, although more slowly. Due to the rigid nature of the silica gel structure and the presence of surface methyl groups, it seems unlikely that neighboring iron centers are able to contact one another or to form oxo-bridged species. The preparation of supported iron(II) complexes with even lower surface concentrations of iron would be of interest to help confirm that neighboring iron centers are not interacting. Silica gel loadings of 1 ligand/50 surface Si (0.05 mmol ligand/g [SG]) or even 1 ligand/100 surface Si (0.01 mmol ligand/g [SG]) would be worthy of investigation. At such low concentrations it would be difficult to obtain Mossbauer spectra, so the distinct color change observed upon oxidation from iron(II) to iron(III) would be the most convenient method of determining whether that oxidation is occurring upon exposure of the [SG]-Fe(II)SalDPT to air. Even at low metal complex surface concentrations, the purple/pink

iron(II) color and the tan/brown iron(III) color should be readily distinguishable on the silica gel.

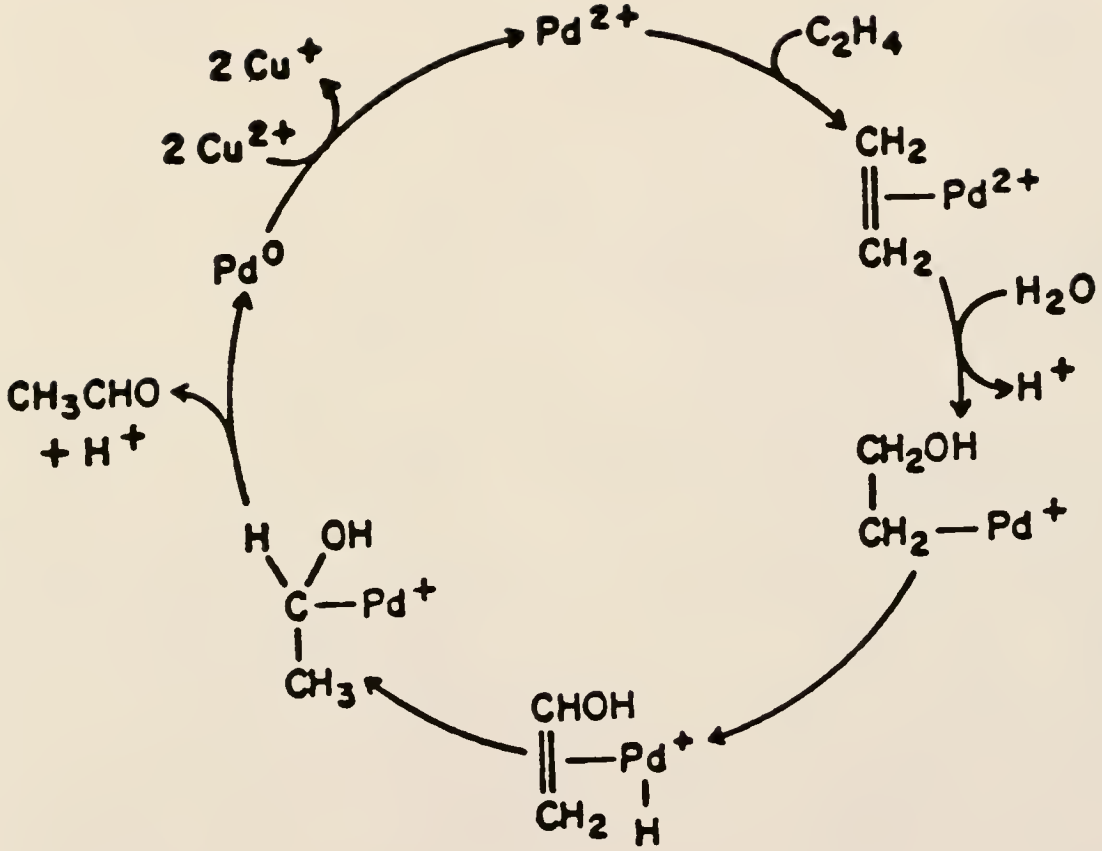
The preparation and characterization of an iron(II)-multidentate complex supported on a rigid inorganic polymer, silica gel, has been accomplished. The possibility of achieving reversible O_2 binding may be reached by this system with further "fine-tuning" of the surface. Application of the rather detailed information of the silica surface and of effects of surface modification described in Chapter III should be of use in future studies of this iron(II) system.

Incorporation of an Active Metal into a Functionalized Support

The design of polymeric supports and of ligands to immobilize catalytic species has been discussed and demonstrated in earlier sections. A logical extension of this concept is to incorporate one metal of a bimetallic catalytic system into the support material while retaining the ability to functionalize the support leading to the immobilization of a second metal species on the support surface.

The Wacker process[25,26] referred to in Chapter II is a well-known bimetallic system utilizing copper and palladium complexes. The general mechanism for this process is shown in Figure 20. The Mimoun system discussed at length in Chapters I and II is a bimetallic system using copper and rhodium complexes. Interest in these two systems was the

Figure 20. General catalytic cycle for the Wacker process.


Pd2+
C2H4
CH2
Pd2+
CH2
H2O
H+
CH2OH
CH2 — Pd+
CHOH
Pd+
CH2 H
CH3
C — Pd+
H OH
CH3CHO
+ H+
Pd0
2 Cu+
2 Cu2+

primary justification to attempt to incorporate Cu(II) ions into silica gel.

Copper(II) ions when mixed with plain silica gel in water have no reaction with the silica surface. However, silica gel treated with dilute aqueous hydroxide solution, which is then thoroughly rinsed with water, reacts with aqueous $Cu(NO_3)_2$ to produce enough copper(II) on the surface to give the entire silica gel a pale blue color. The hydroxide solution presumably ensures that the silica surface reaches its maximum concentration of surface $-SiO^-Na^+$ groups. When the hydroxide treated silica gel is mixed with excess $Cu(NO_3)_2$, most of the copper ions do not stay on the silica gel, but enough react to give the gel a very distinct blue color. Techniques were later used to estimate the amount of copper on the surface (vide infra). However, extensive Soxhlet extraction of the silica gel with boiling water does not remove copper ions, confirming that the copper is well bound to the surface.

Silica gel was prepared with an anion exchange capability with general formula $[SG]-OSi(CH_2CH_2CH_2)N(CH_3)_3I$. Details of these types of silica gels and their preparation will be discussed in a later section. These samples can then be rinsed with hydroxide and treated with copper(II) ions. The typical blue copper color is then evident in the resulting gel. The fact that some of the iodide ions on the silica gel surface may be replaced by hydroxide ions during this procedure does not matter in this application. The

anion exchange silica gel with copper ions incorporated is then able to react with K_2PdCl_4 producing a green silica gel with tetrachloropalladate ions exchanged onto the surface.

Homogeneous palladium(II)/copper(II) Wacker oxidations were conducted using 1-hexene substrate yielding 2-hexanone product. The homogeneous reaction was conducted at 70°C, 40 psi O_2 in an aqueous DMF solvent with 0.06 mmol of both metals producing approximately 30 turnovers in 24 hours. The heterogeneous oxidation was then conducted using the silica gel with Cu^{2+} on its surface and palladium bound to it. The conditions used were equivalent to those for the homogeneous reaction, with approximately 0.07 mmol of palladium supported on the silica gel. It is difficult to estimate the amount of copper on the surface, it being the amount which is bound after the surface is treated with NaOH. This heterogeneous catalyst produced roughly 0.5 turnovers initially and then did not yield any further product over a long time period. There was no visible change to the silica gel catalyst.

The initial activity of the silica gel supported catalysts is a positive result. Leaching experiments indicate no activity in solution, so that any activity observed is due to metals supported on the surface. One possible factor limiting activity is that the palladium complex is at the end of a relatively long chain of atoms which bind it to the silica surface, while the copper ions are located on the silica surface. The physical separation between palladium and copper may well limit long term

catalytic activity. Normally one would predict that lack of Pd/Cu contact would result in the production of reduced metallic palladium and an accompanying grey/black color change. In this case it is uncertain whether such a color change would be visible due to the loading of the surface with blue copper ions, and the low concentration (one palladium ion per every 75 surface silanol groups) of surface palladium. In this case, rather than site isolation, higher surface loadings may improve activity.

Electron spectroscopy for chemical analysis (ESCA) was employed to provide some information about the functionalized silica surface. This work was done at the Major Analytical Instrumentation Center (MAIC) of the University of Florida through the assistance of Susan Hofmeister. The x-ray photoelectron spectra resulting from a study of the Pd/Cu silica supported system described above indicate the presence of very small amounts of copper. Although ESCA is not a precisely quantitative method, it does indicate the relative amounts of species on a solid's surface. Since ESCA can examine at the most a depth of 100 Angstroms on a surface, this result would tend to indicate, despite the definite blue color of the silica gel, a relatively low loading of copper on the silica surface. This led to attempts to incorporate copper ions into silica gel (vide infra) and suggested that increased loadings of palladium may also be needed.

Apparently low loadings of copper ions on the silica gel surface led to attempts to produce silica gel having copper incorporated throughout the silica structure. The approach taken was that of dissolving the silica gel and then reforming the solid with copper ions interspersed in the silica gel. The technique of dissolving silica gel in acid (HCl), adding $Cu(NO_3)_2$, and neutralizing with base (NaOH) produces a very blue silica gel which does not change after extensive aqueous washings and extractions. The drawback to the copper incorporated silica gel produced is that it surface area is very much lower than that of the initial reactant silica gel. All of the experiments conducted support the validity of the chemical principles utilized in this approach. However, in discussions with chemists from W. R. Grace (manufacturers of Davison brand silica gel) the rather sophisticated technology involved in production of high surface area silica gel was revealed.[86] It is uncertain whether conditions sufficient to produce high surface area silica gel can be obtained with materials available at a typical academic laboratory. Industrial collaboration may be worthwhile in order to produce a high surface area silica gel with a metal ion incorporated into the silica gel matrix. Surface functionalization in the usual manner should then be possible ultimately yielding a bimetallic system with both metals in and on a solid heterogeneous catalyst.

Synthesis of a Silica Gel Anion Exchange Resin

Anion exchange resins are commercially available through several companies. However, they are virtually all composed of polystyrene or other similar organic polymers. The drawbacks to these substances are their lack of rigidity and their inability to tolerate increased temperatures. Polystyrene itself begins to soften at 85°C, and also has solvent dependent swelling properties.

An anion exchange capability on silica gel was prepared by first putting an amine moiety on the surface. The surface is also covered with $-Si(CH_3)_3$ groups in order to achieve site isolation of the other groups and in order to help protect the surface O-Si bonds of the functional groups from hydrolysis. The amine groups are then reacted with chloromethane in order to produce quaternary ammonium chloride functionality on the surface. The analogous quaternary ammonium iodide silica gel can be prepared by reacting iodomethane with the supported amine.

The silica gel anion exchange resin reacted as would be predicted in all of the applications in which it was used. The gel picked up $PdCl_4^{2-}$ ions as described previously. The functionalized silica gel was shipped to the Sybron Corporation where testing is being conducted to determine how well this substance meets industrial criteria for a good anion exchange resin. Initial results appeared encouraging, but final results have not been reported.

The surface loading on the silica may be easily varied to accommodate different applications. Lower loadings would allow site isolation of species such as metal complex, while higher loadings would of course provide the capacity to bind larger quantities of an anion from solution. Silica gels of several loadings were prepared. Due to the nature of silica gel, each sample is independent of swelling problems and is stable at much high temperatures than polystyrene resins.

Titanium Carbide as a Solid Support

The stability of any substance bound to a solid support is ultimately related to the strength of the bond from the surface of the support to the species attached to that surface. The presumption that bonds of carbon or carbanions to metal centers might be significantly stable led to an investigation of titanium carbide (TiC) as a support material.

Titanium carbide is very unreactive and so initial attempts were made to alter the surface in order to generate active surface species. Halogenation of the surface was attempted by the passing of chlorine gas over TiC contained in a tube furnace. Temperature of 150°C - 350°C during exposure produced liquid $TiCl_4$ along with black TiC of unknown surface composition. Gradual heating up to 150°C yielded no $TiCl_4$ liquid.

Based on an estimation of the very small particle size of titanium carbide, it is calculated that even complete

chlorination of the surface would yield a very small percent of chlorine by weight which could not be measured by any normal elemental analysis technique. Thus, it is difficult to determine whether any chlorine atoms have been bound to the carbide surface after treatment with chlorine. Several unsuccessful attempts were made to react other species with the alleged surface chlorides. The stirring of n-butyl lithium in hexanes with chlorinated TiC, followed by addition of the $Rh(CO)_2^+$ cation in THF was an attempt to place an active metal center on the carbide surface. However, the resultant solid was inactive for the oxidation of 1-hexene with copper(II) added into solution under O_2 pressure (40 psi) at 70°C in ethanol solvent. As discussed earlier (Chapter III), rhodium centers supported on silica gel under similar conditions successfully oxidize 1-hexene to exclusively 2-hexanone. Attempts to hydrogenate 1-hexene (as solvent) under 50 psi H_2 pressure at 45°C by the same "TiC-$Rh(CO)_2$" solid were also unsuccessful. The chlorinated titanium carbide was stirred in a nitrobenzene solution saturated with ammonia in an attempt to attach an $-NH_2$ functionality to the carbide surface. No adequate technique was found to quantitate the small amount, if any, of surface amine produced. Attempts to titrate the surface amine with acid were also unsucccesful. Liquid bromine was stirred with plain titanium carbide in an effort to achieve bromination, rather than chlorination, of the carbide surface. Here again, the problem faced was that of determining the exent of

reaction that had occurred. Each of the approaches tried with the chlorinated carbide was also used with the brominated samples, producing equally unsuccessful results.

It was decided that more detailed knowledge of the carbide surface is required to aid future attempts at functionalization. As a result, ESCA studies of the plain titanium carbide surface were conducted indicating at least two different types of surface titanium atoms and more than one type of surface carbon species. The overall ESCA spectrum of titanium carbide is shown in Figure 21. An expanded version of the carbon region of the spectrum reveals two different types of carbon present and is represented in Figure 22. The peak on the left represents carbon atoms which are bound to oxygen or other carbon atoms, while the peak on the right represents carbon atoms bound to titanium. The titanium region of the ESCA spectrum shown in Figure 23 reveals at least two different types of titanium species present. The ESCA technique provides a general indication of relative amounts of surface species measured. Thus, all further surface reactions on the carbide support should be monitored by ESCA methods to determine the type and quantity of resultant surface species. Other methods which yield more accurate quantitative data are also available at the Major Analytical Instrumentation Center, and these may also be employed as needed.

Figure 21. ESCA spectrum of titanium carbide (TiC) shown as intensity (I) versus binding energy (B.E.).

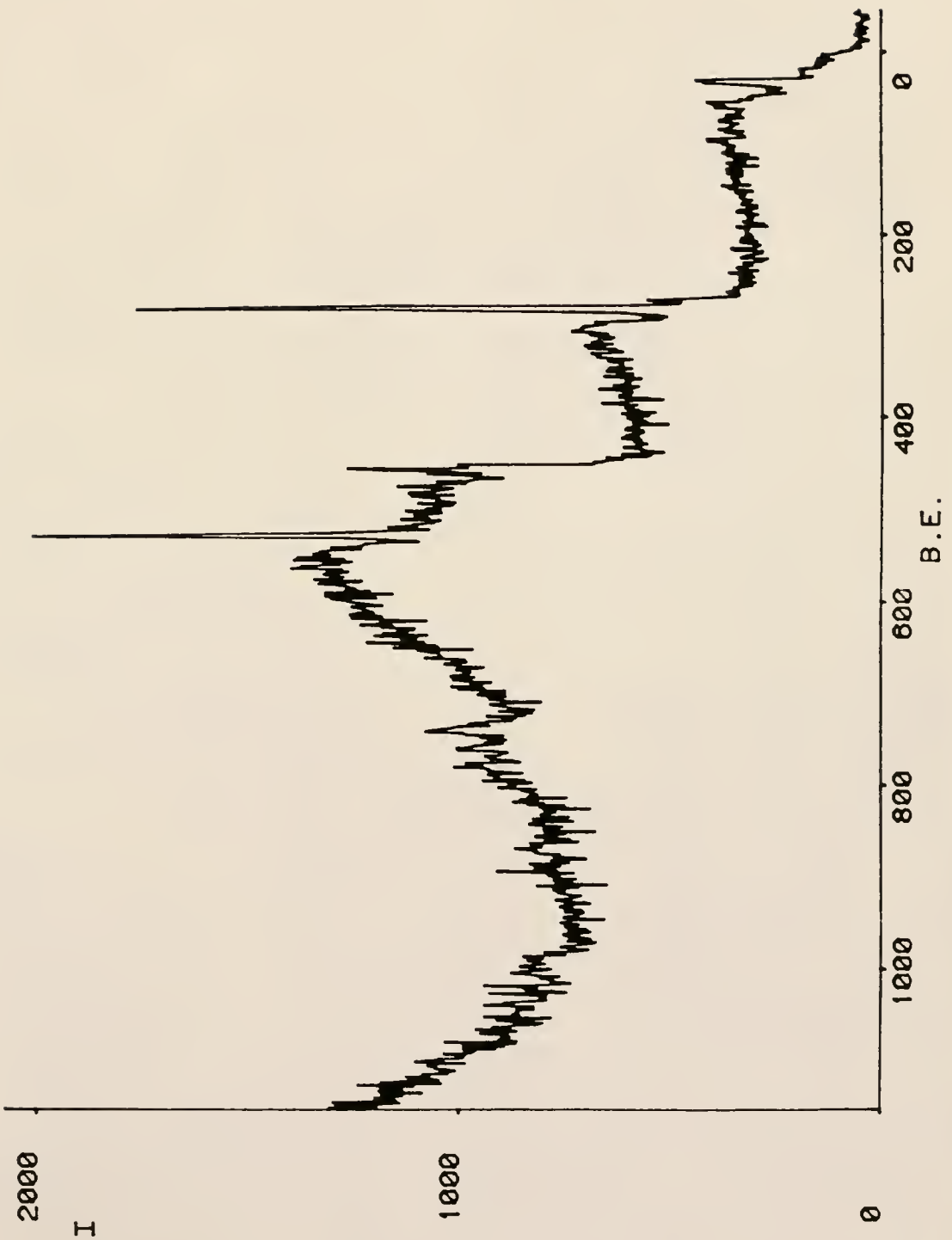

2000
1000
0
I
1000
800
600
400
200
0
B.E.

Figure 22. Carbon region of the ESCA spectrum of TiC.

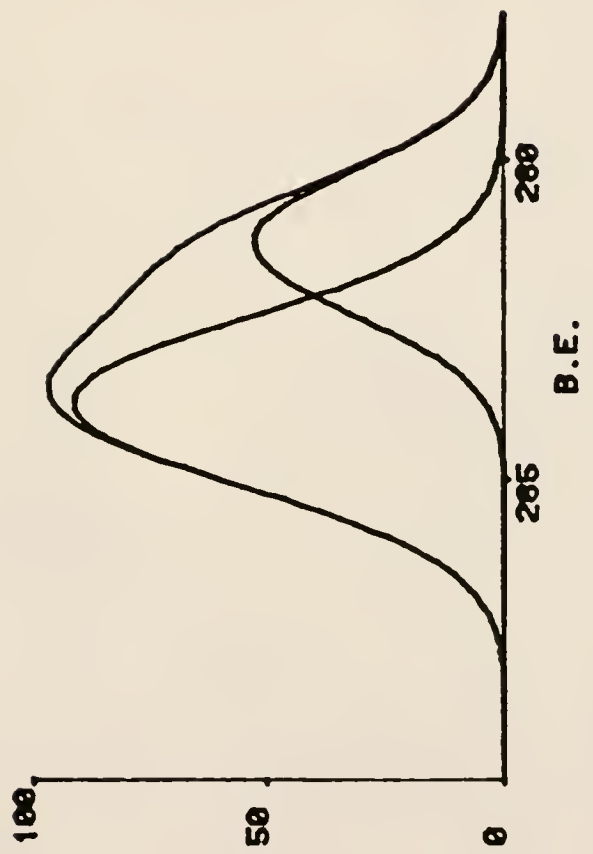
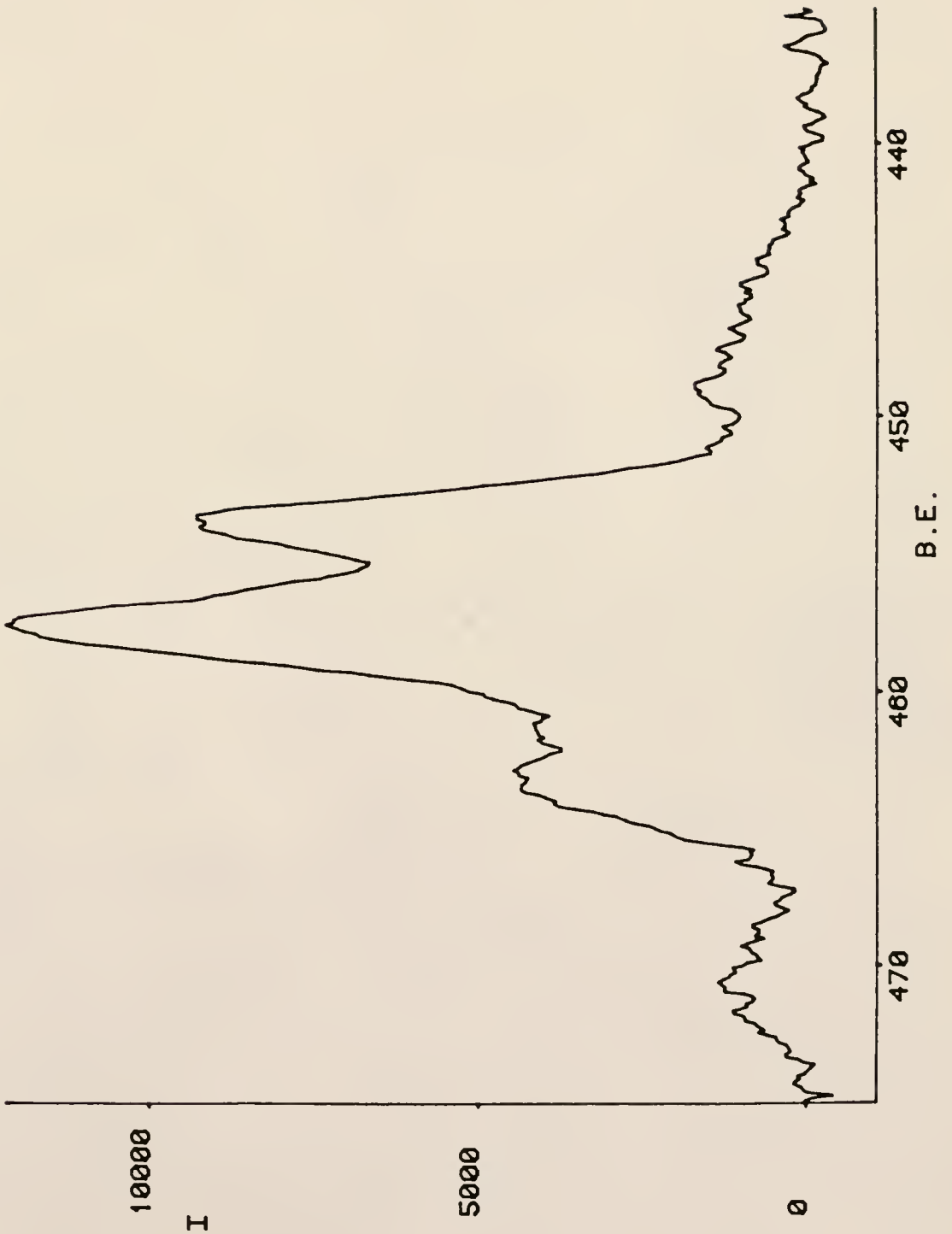

100
50
0
205
200
B.E.

Figure 23. Titanium region of the ESCA spectrum of TiC.


I
10000
5000
0
470
460
450
440
B.E.

Fenton Chemistry

The conversion of isopropanol to acetone and 1,2-propanediol is one example of the so-called Fenton chemistry.[80] This conversion was accomplished by aqueous solutions of either $FeCl_2 \cdot 4H_2O$ or $FeCl_3$ (one mmol) at room temperature in the presence of aqueous 0.1 N $HClO_4$ and hydrogen peroxide. Attempts were made to use [SG]-Fe(III)SalDPT as a heterogenous model to achieve the same reactivity. However, leaching of the iron complex off of the silica gel support occurs under reaction conditions identical to those described above. The silica gel completely loses its brown color and a white gel is produced. Addition of hydroxide ion to the colorless filtrate after reaction produces a rust colored precipitate, presumably an iron oxide compound. The silica gel supported iron(III) complex is the presence of all starting materials except H_2O_2 does not completely leach into solution, as a pale brown color remains on the gel. Hydroxide ion again confirms the presence of iron in solution. It seems that leaching by acid alone is not as complete as the metal loss in the presence of both acid and hydrogen peroxide. The estimation of leaching was based simply on the color changes involved, primarily loss of color from the silica gel. If the amounts of leaching had been small, some attempt would have been made to quantitate the amount of iron leached into solution. However, in all of the cases studied the amounts of leaching were quite large.

The use of pure isopropanol and of several different isopropanol/water mixtures as solvents, as well as acetonitrile solvent, produced no observable reduction in loss of iron complex from the silica surface. The silica gel samples tested had all of their available surface covered with trimethylsilyl groups in an unsuccessful attempt to protect the surface functional groups from hydrolysis under these conditions. Systems which require the use of acid and hydrogen peroxide are seemingly going to be very difficult to catalyze by silica gel supported species. It is not known whether any other surface groups would be able to better protect silica supported functional groups under similar conditions.

Experimental

Silica Gel

Silica gel employed in all of the following experiments is Davison Grade 62 silica gel from W. R. Grace. This silica gel has a wide pore diameter of 14 nm, a specific area of 340 m^2, and a pore volume of 1.1 cm^3/g as stated on the label of the container. Maximum surface reactivity of the silica gel is achieved by washing the silica gel with dilute acid (0.1 M HCl) followed by thorough drying at 100^{o}C under vacuum. The silica gel retains its very white color throughout the above washing procedure.

Functionalization of Silica Gel with 1-trimethoxysilyl-2-(p,m, chloromethylphenylethane)

The silane, $(H_3CO)_3Si(CH_2CH_2C_6H_4CH_2Cl)$, was purchasd from Petrarch Systems, Inc. The acid washed silica gel, 30 g, was placed in a 500 mL round bottom flask fitted with a condensor and argon inlet. Xylenes, 225 mL, were stirred with the silica gel with argon bubbling in from a plastic needle for 45 minutes to an hour. An addition funnel with another 75 mL of xylenes solvent was degassed with argon from a separate argon inlet simultaneously. The appropriate amount of silane was syringed into the addition funnel, along with chlorotrimethylsilane if alkylation of the silica surface is also desired. The silanes are then added dropwise to the silica gel slurry which has been heated to near reflux under an argon atmosphere. After addition (1-2 hours) the slurry is stirred at gentle reflux overnight.

The following day the silica gel is cooled, then filtered in air and washed with xylenes, benzene and methanol. The silica gel is then Soxhlet extracted for 24 hours with benzene. The gel is finally dried at 70-80^{o}C under vacuum. This functionalized silica gel will be referred to as [SG]-$PhCH_2Cl$.

Preparation of Silica Gel Bound 3,3'-Iminodi-propionitrile

The nitrile, $HN(CH_2CH_2CN)_2$, was purchasd from Kodak. A sample of [SG]$PhCH_2Cl$ (9-10 g) as described in the previous

section was placed in a Parr pressure bottle with 30-35 mL of 3,3'-iminodipropionitrile and a magnetic stirring bar. This was attached to a pressure head identical to that used for catalysis (see Chapter II) except for its attachment to an argon cylinder. The silica gel slurry was purged 8 times with 80 psi Ar, then set to 90 psi Ar and placed in a 90°C oil bath for 24 hours. Vapor pressure of the nitrile causes the pressure to increase, but is vented if necessary to keep the total pressure at 100 psi.

After one day, the slurry is cooled and the argon pressure removed. Placing 20-30 mL methanol into the pressure bottle and letting stand for a short while facilitates filtering, which is best done on a Buchner funnel with filter paper rather than a fritted filter. The silica gel is washed with methanol, benzene and then more methanol followed by Soxhlet extraction for 24 hours with methanol. The silica gel is then dried at 70-80°C under vacuum.

Preparation of Silica Gel Bound bis-(3-aminopropyl)-amine [SG]-DPT

A sample of silica gel containing cyano groups on the surface as described in the previous section was placed into a 500 mL 3 neck round bottom flask with a stir bar. Cycles of evacuation and N_2 filling were alternated, followed by syringed addition of 1 M BH_3/THF solution (200 mL for a 25 g sample). If the silica gel sample used has not been thoroughly dried of methanol, a bubbling borane-methanol

reaction will be observed upon BH_3/THF addition. The silica gel is stirred in the borane solution for 24 hours under a nitrogen atmosphere. The slurry is then heated to near reflux for 2 hours, allowed to cool followed by the addition of enough methanol to destroy all of the excess borane. The mixture is again heated to near reflux for 1-2 hours, cooled and filtered in air.

Washing procedure on a polymer such as polystyrene would entail treatment with acid while heating, washing and then treatment with base. However, there is a fear of hydrolyzing the functional groups off of a silica surface with acid. As a result, THF and toluene were used to wash the filtered silica gel. Dilute (0.1 M) HCl in dioxane was then used to briefly treat the silica gel, then washed, and finally pyridine in dioxane stirred with the silica gel. Finally, thorough washing with methanol was done followed by drying at 50-60^{o}C under vacuum. Later experiments indicated that heating with 3 M HCl/dioxane probably does remove the functional groups from the silica surface as indicated by its inability to react with salicylaldehyde (the next step) or to incorporate copper(II) ions.[87]

Condensation of Salicylaldehyde with [SG]-DPT

Benzene is added to [SG]-DPT to make a slurry, followed by addition of a large excess of salicylaldehyde and several hours of stirring, although reaction occurs very quickly.

The slurry is also heated for an hour to insure complete reaction. The product with salicylaldehyde incorporated, [SG]-SalDPT, is washed with benzene and ethanol thoroughly, and then dried under vacuum at 60°C. The product silica gel is a bright yellow in color due to the yellow Schiff base.

Incorporation of Metal Ions into [SG]-SalDPT

Several metal ions are incorporated into the bound [SG]-SalDPT ligand by stirring the functionalized silica gel with a DMF solution of the metal ion. Iron(III) chloride in 1:1 (v:v) DMF/pyridine and cobalt(II) acetate in DMF are used to prepare [SG]-Fe(III)SalDPT and [SG]-Co(II)SalDPT, respectively. The cobalt(II) analog is prepared under argon, but both Fe(III) and Co(II) analogs are air stable. Copper(II) acetate in DMF is used with the [SG]-DPT ligand to prepare the [SG]-Cu(II)DPT complex. In each case the silica gel ligand and metal ion solution are stirred overnight, filtered and thoroughly washed or Soxhlet extracted.

The [SG]-Cu(II)DPT and [SG]-Co(II)SalDPT·O_2 (oxygen adduct) both give characteristic ESR spectra similar to those of their homogeneous analogs.

Incorporation of Fe(II) into [SG]-SalDPT

The Fe(II) supported complex preparation procedure is quite air sensitive, and much care must be employed to exclude oxygen. Distilled DMF (30 mL) is added to 2.0 g [SG]-SalDPT or [SG]-BrSalDPT and the slurry freeze-pump-thawed

many (at least five) times. This is seemingly the best way to exclude oxygen from the initial silica gel ligand. The source of iron is $Fe(CO)_5$, which is poured through glass wooland then placed under a nitrogen atmosphere. The $Fe(CO)_5$ (2 mL) is syringed into the silica gel slurry and stirred overnight in the dark, under inert atmosphere. The next day the slurry (deep red in color) is heated for 3-4 hours (not to reflux). The slurry turns a deep purple color during heating. The slurry is cooled, then filtered in a Schlenk apparatus which has been attached to the round bottom flask throughout reaction. The silica gel was washed with DMF, then the entire apparatus was transferred into an inert atmosphere glove box. Here the silica gel is washed with DMF, THF and diethyl ether until clear filtrates are obtained. The pink silica gel is then dried under vacuum for 24 hours, and stored in the inert atmosphere box. The colors during preparation and of the final solid correspond to those found from similiar work conducted on polystyrene.[83] Mossbauer simulations were done by program DMOSFIT[88] with nuclear energy levels calculated using spin Hamiltonian calculated data points fitted to experimental data using the non-linear least squares program DSTEPIT.[89]

Incorporation of Cu(II) into the Silica Gel Matrix

Davison Grade 62 silica gel, washed with 1 M NaOH, and then copious amounts of water, is stirred with a copper(II) nitrate solution for 24 hours. The resulting blue silica gel

can then be Soxhlet extracted with boiling water for several days without the appearance of any blue copper ions in the extraction water. This procedure places copper ions on the silica surface.

Silica gel is dissolved in concentrated hydrochloric acid in the first step to incorporating copper ions into the silica gel. Excess $Cu(NO_3)_2 \cdot 3H_2O$ is added to the solution and stirred for several hours. The solution is then neutralized to pH 7 with large amounts of NaOH solution. Upon reaching a pH of 7, the green solution turns to cloudy blue as solid is formed. After 2 hours the solid is filtered and washed with copius amounts of water. This very bluesolid is dried under vacuum to yield a rather brittle, non-uniformly sized silica gel. This resulting silica gel appears to have copper ions as part of its structure, but its surface area has been greatly reduced as evidenced by the large chunk-like nature of the resulting solid. Extensive physical crushing of the solid produces irregularly shaped, brittle pieces which do not approach the small homogeneous grain-like nature of the original silica gel.

Preparation of Silica Gel Anion Exchange Resins

Plain silica gel is reacted with $(CH_3CH_2O)_3Si(CH_2CH_2CH_2NH_2)$ and $ClSi(CH_3)$ (if desired) in xylenes in the same manner as was described earlier in preparing chloromethylphenyl silica gel. The functionalizing silanes are added from an addition funnel dropwise into a slurry of the silica

gel in xylenes which has been heated nearly to reflux. An amount of 2.8 mL (12 mmol) or 28.0 mL (120 mmol) of the aminosilane may be reacted with 60 grams of plain silica gel to yield products having 0.2 mmol $-NH_2$/g [SG] or 2.0 mmol HN_2/g [SG], respectively. Some amount of $ClSi(CH_3)_3$ may also be added to react with a percentage of the remaining surface silanol groups (11.7 mL to react with all of the remaining -SiOH groups). After 24 hours of reaction, the silica gel is cooled, filtered and washed with xylenes, ethanol and benzene. Soxhlet extraction in benzene and the usual vacuum drying follow.

The resultant silica gel is then stirred overnight at room temperature with a DMF solution which has been saturated with CH_3Cl gas. Also added to the slurry is a small amount of 2,6-dimethylpyridine (2,6-lutidine) to act as a proton sponge. Filtering, washing with acetone and benzene, and drying under vacuum produce a silica gel with a quaternary ammonium chloride functionality bound to the surface. A quaternary ammonium iodide functionality is produced in an identical manner by substituting iodomethane for chloromethane above. These silica gels are then able to function as anion exchange resins.

Titanium Carbide as a Solid Support

Titanium carbide was purchased from Aldrich and used without further purification. A tube furnace was used with a quartz tube with a three-way stopcock at one end and a two-

way stopcock at the opposite site. Titanium carbide was placed in the center of the tube and purged with nitrogen, the outlet end being attached to a bubbler. Chlorine gas from a lecture bottle was slowly passed over the carbide solid as the tube was slowly heated to 125°C for two hours, then heated to 150°C for another hour. Other experiments where the solid is heated to 250°C (or 350°C) produces a clear liquid which fumes vigorously upon exposure to air characteristic of $TiCl_4$. The black solid is filtered and washed with toluene. Both of the products described above were used in further reactions as chlorinated titanium carbide. These samples were stirred in a nitrobenzene solution saturated with NH_3 in an attempt to produce amine groups on the surface. The chlorinated samples were also treated with n-butyl lithium in hexanes under argon, followed by reaction with $[Rh(CO)_2(solvent)_n]BF_4$ in THF in an attempt to bind the rhodium complex to the carbide surface. As described in the Results and Discussion Section, no adequate technique was employed to determine the success of these reactions.

Bromine was also reacted with titanium carbide in attempts to produce bromine atoms bound to the carbide surface. Liquid bromine was stirred with titanium carbide for 24 hours and then thoroughly washed with toluene. Soxhlet extraction is strongly recommended in these systems to remove reactants from the solid. Reaction schemes similar

to those carried out on the chlorinated carbide samples were also conducted on the brominated carbides.

Fenton Chemistry

The substances $FeCl_2 \cdot 4H_2O$ (0.240 g) and .50 mL aqueous 0.1N $NClO_4$ are mixed together and degassed with N_2 into which 1.1 mL isopropanol (2-propanol) is syringed followed by 0.1 mL 30% H_2O_2. This mixture is stirred under N_2, aliquots withdrawn and examined by GLC (DEGA column, 100°C). The same procedure is employed using $FeCl_3$ as the iron source.

The materials 0.18 g [SG]-Fe(III)SalDPT (0.5 mmol ligand/g [SG]), 50 mL 0.1N $HClO_4$, 1.1 mL isopropanol and 0.5 mL 30% H_2O_2 were used for supported reactions. After 24 hours of reaction, both the silica gel and filtrate were colorless. Addition of hydroxide ion to the filtrate produced a rust colored precipitate.

Into large screw top vials were placed 0.1 g samples of [SG]-Fe(III)SalDPT, 5 mL of 0.1N $HClO_4$ prepared in the solvent of choice, and 0.0 to 0.5 mL of aqueous 30% H_2O_2. The choice of solvent (water, isopropanol, several water/-isopropanol mixtures, acetonitrile) had very little effect on the extent of leaching, at least within the limits of comparing color change by eye. The acid-only systems showed markedly less leaching than did the acid/peroxide samples. The silica gel samples treated with both acid and peroxide were either completely white or very slightly brown after 24 hours, showing complete or nearly complete loss of metal from the silica support.

CHAPTER V
GENERAL CONCLUSION

Throughout the previous chapters, research which involved the use of transition metal centers as oxidation catalysts has been described. The importance of careful characterization of the active catalytic species in a system has been presented. Also demonstrated has been the need to obtain detailed knowledge of the surface in preparing immobilized, catalytically active species on an inorganic polymer such as silica gel. Applications to several ligand systems and transition metals were presented, and the potential for further expansion of this research pointed out.

Specific, detailed chemical conclusions were presented with each topic as it was discussed. Overall, the goal of this work has been to provide some insight into the nature, design, support, application and refinement of several transition metal oxidation catalysts.

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30. When the mixture was in ethanol for 96 hours the electronic absorption band for $RhCl_3 \cdot 3H_2O$ at 510 nm shifts to 483 nm which is very similar to that found for C (at 480 nm). This possibly may be due to a substitution of one H_2O in $RhCl_3 \cdot 3H_2O$ by an ethanol molecule.

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33. This reaction is so slow with t-BuOOH that only a low concentration of analogous intermediate builds up, and the electronic absorption band due to it is only poorly resolved. Therefore, we have not obtained an accurate measure of its energy.

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37. It is possible that trace amounts of metals which may be present in the absolute ethanol or isopropyl alcohol solvents are also catalyzing HOOH production. However, Bronsted acid undoubtedly plays a role due to the dependence on $[H^+]$ found in eq. 9.

38. The measurement of small amounts of acetone production by GLC was not extremely accurate due to the presence of some acetone in our isopropyl alcohol solvent. Cu(II) was only active over the first 30 min due to its reaction with the acetone produced.

39. The band in the electronic absorption spectra due to the rhodium(III) trichloride prepared in acetone was poorly resolved due to the concurrent acid-catalyzed aldol condensation of acetone under these conditions. This latter reaction produced a band of its own in the electronic spectra which overlapped that for the rhodium(III) trichloride.

40. This latter explanation is somewhat speculative due to the poor resolution, as was the case for the t-BuOOH adduct (see ref. 7).

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Professor of Chemistry

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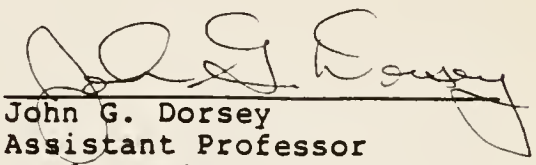

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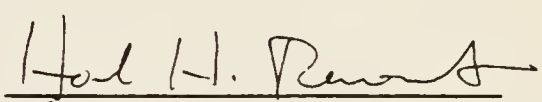

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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